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Investigation of New Techniques for Control of Smelter Arsenic Bearing Wastes. Volume I Experimental Program

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16. ABSTRACT

In 1976, the Industrial Environmental Research Laboratory at Cincinnati sponsored a research program at the Mineral Research Center, Montana Tech Alumni Foundation, to investigate a variety of approaches to the fixation of arsenic bearing wastes, particularly smelter flue dusts, to render them harmless to the environment. The enclosed document reports the findings of this work.

A comprehensive program was undertaken to investigate various methods of fixing arsenic bearing flue dust wastes produced in smelting of nonferrous metal concentrates. The program was comprised of three principal elements: (1) separation of the arsenic from metal values by leaching; (2) incorporation of the arsenic into a fixation matrix; and (3) leach testing of samples of the fixed product to determine suitability for environmental protection.

Stabilization of the arsenic by incorporation in slag matrices and in cements, mortars, clays, and concrete was investigated. The most promising technique found was stabilization by dissolution in the slag matrix to form a solid solution upon cooling.

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INVESTIGATION OF NEW TECHNIQUES FOR CONTROL OF SMELTER ARSENIC BEARING WASTES
VOLUME I
EXPERIMENTAL PROGRAM

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The primary nonferrous metals industry is the sole source of arsenic production and the principal source of arsenic released to the environment. In 1976, the Industrial Environmental Research Laboratory at Cincinnati sponsored a research program at the Mineral Research Center, Montana Tech Alumni Foundation, to investigate a variety of approaches to the fixation of arsenic bearing wastes, particularly smelter flue dusts, to render them harmless to the environment.

A comprehensive program was undertaken to investigate various methods of fixing arsenic bearing flue dust wastes produced in smelting of nonferrous metal concentrates. The program was comprised of three principal elements: (1) separation of the arsenic from metal values by leaching; (2) incorporation of the arsenic into a fixation matrix; and (3) leach testing of samples of the fixed product to determine suitability for environmental protection.

Stabilization of the arsenic by incorporation in slag matrices and in cements, mortars, clays, and concrete was investigated. The most promising technique found was stabilization by dissolution in the slag matrix to form a solid solution upon cooling.

David G. Stephan
Director
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ABSTRACT

A program of leaching experiments was organized to investigate the solubility characteristics of a variety of arsenic-bearing flue dust materials collected from domestic primary producers of copper, zinc, and lead. Leaching experiments were conducted using six conventional lixiviants (water, sulfuric acid, ferric sulfate, ferric chloride, aqueous ammonia, and sodium hydroxide) in various combinations. Leach extraction was determined as a function of time, temperature, and reagent concentration.

Results of the leaching tests indicated that up to 99 percent of the contained arsenic in several of the dusts examined could be solubilized by at least one of the lixiviants tested under appropriate conditions. Due to the complex and variable mineralogy of the arsenic in the dusts examined, no universally effective method of leaching capable of complete dissolution of arsenic was found. The complexity of both the chemical and mineralogical compositions of smelter flue dusts also results in widely dissimilar solubility characteristics of other heavy metal constituents giving rise to a wide range of solution treatment problems following leaching. All leach tests performed resulted in the dissolution of significant amounts of copper, iron, zinc, cadmium, antimony, and tellurium in addition to arsenic.

A program of solution purification experiments was organized to investigate the potential for recovery and fixation of arsenic from pregnant solutions.

Laboratory tests included precipitation of arsenic by chemisorption: on hydrated ferric oxides generated by hydrolysis of ferric sulfate present in the leach liquor, and on particulate surfaces of phosphate rock, bentonite clay, cement plant cottrell dust, and coal-fired power plant ash. Results of the laboratory tests indicated that arsenic levels of 0.05 parts per million or less were occasionally achieved. However, prolonged solubility tests conducted on arsenical precipitates indicated that resolution of arsenic can be expected to occur, resulting in saturation levels of from 1 to about 20 parts per million.

A program of arsenic fixation experiments was organized to investigate the stabilization of arsenic by dissolution in slag matrices; and by encapsulation in cements, mortars, clays, and concrete. The success or failure of the stabilization was determined by reasonably long term leach tests.

Results of the study indicated that arsenic can be effectively stabilized by first converting it to an arsenate form, then dissolving it in a slag matrix. Further kinetic limitations can be imposed on arsenic release by encapsulating the arsenic bearing slag in cements, concretes, and mortars. Aqueous extraction results indicate minimal release.

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SECTION 1

INTRODUCTION

BACKGROUND

In high temperature operations such as roasting and smelting, evolution of fine dust takes place. This dust is entrained by the moving gases and carried away into the flue system. Most of the particulate matter in flue dust is collected in the flue system by using flue chambers, electrostatic precipitators, and baghouses. Particulate matter is collected at various points in the flue system. The collected dust is received in hoppers. These are the dust origin points. By controlling the velocity, volume, and the temperature of the moving stream; volatile constituents such as As_2O_3 may be made to deposit along with the particulate matter.

In order to understand the origin, handling, recycling, retreating, or storage of the flue dust, it is necessary to understand the copper smelting process. In Figure 1, a flowsheet is presented for the process. A simplified version of the previous flowsheet is presented in Figure 2.

The flue dust can contain high levels of copper, lead, zinc, cadmium, and other valuable metals (Table 1). It also can contain a significant amount of arsenic. Recycling this dust, which

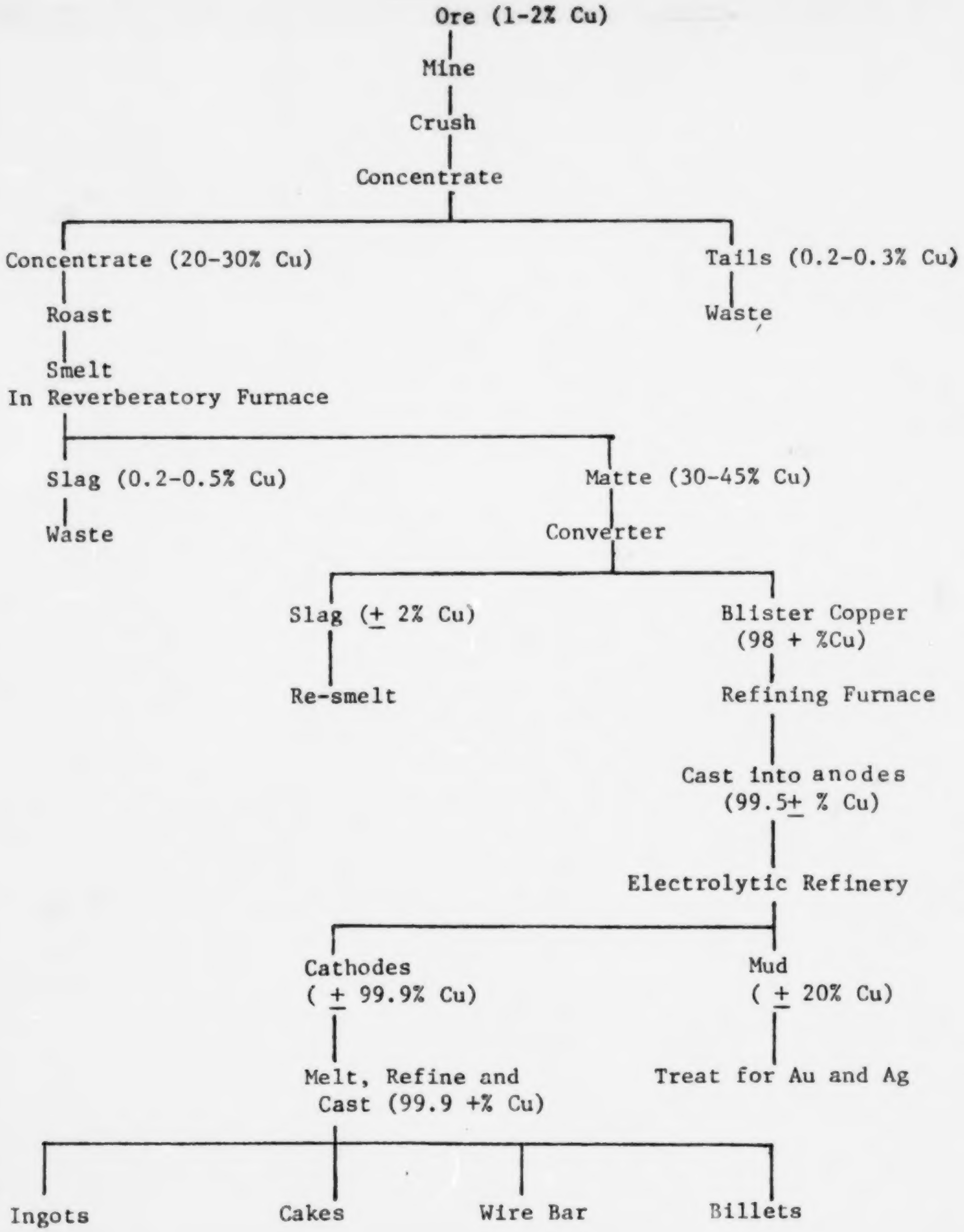


Figure 1. Copper smelting process flowsheet adapted from Hayward 1952 (2).

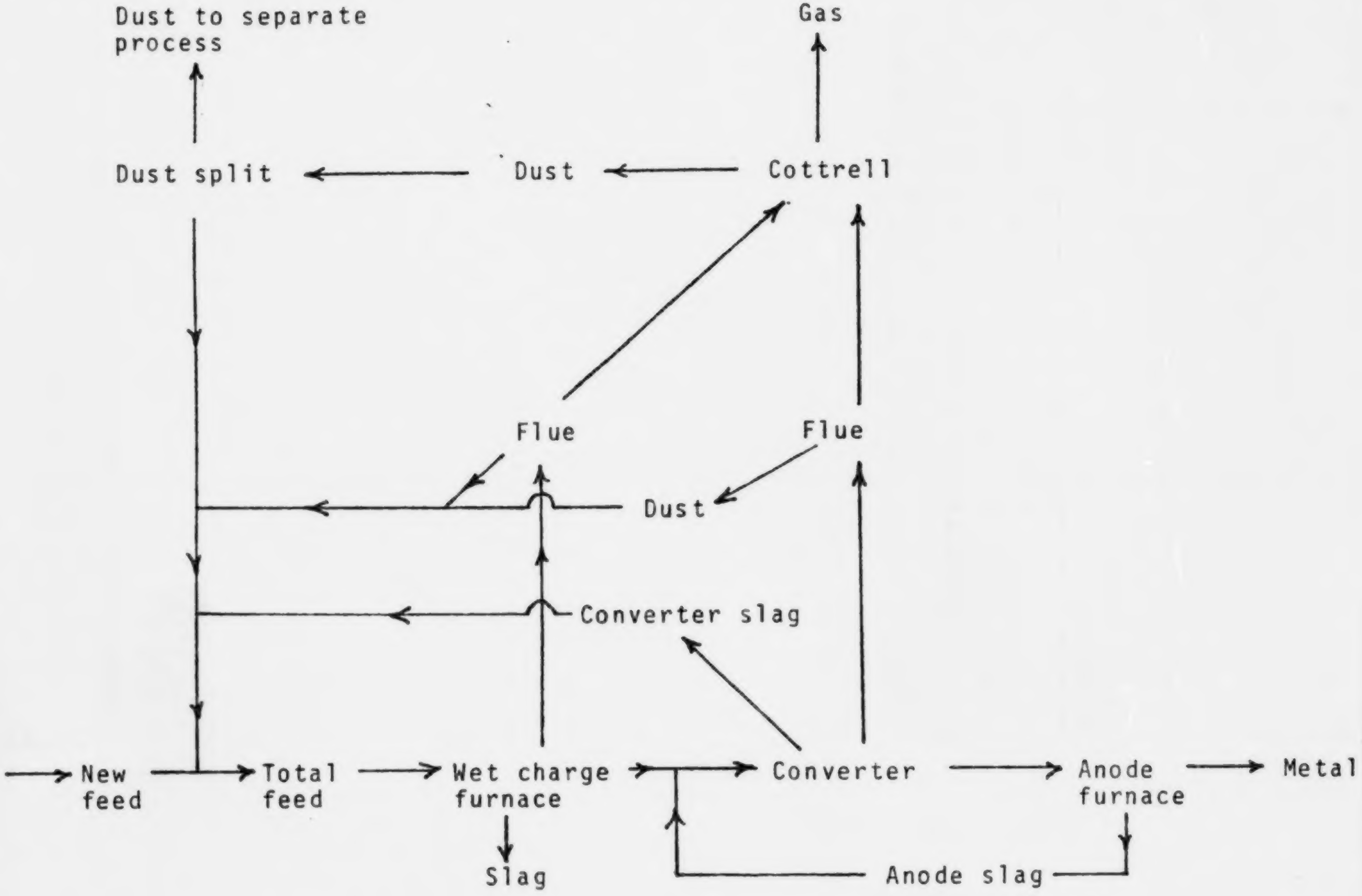


Figure 2. Typical conventional smelter flowsheet.

TABLE 1. COMPOSITION OF THE FLUE DUST*

Element	%
Arsenic	17.5
Copper	8.2
Zinc	5.9
Lead	4.1
Iron	12.7
Cadmium	0.30
Antimony	0.35
Bismuth	0.38
Tin	0.48
Sulfur (total)	9.3
Silver	7.4 oz/t

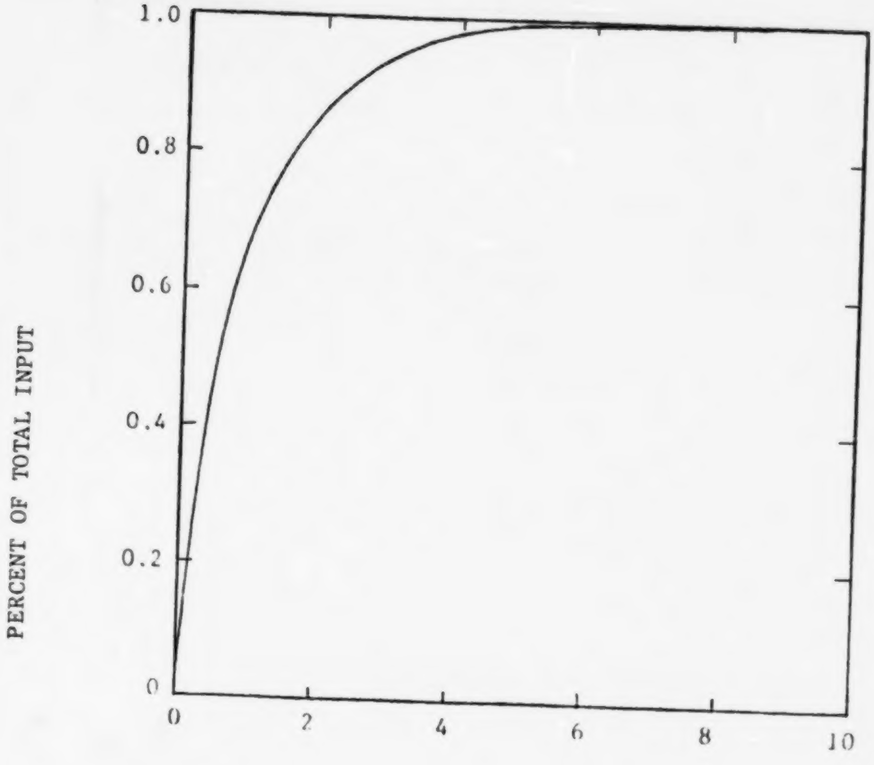
*This sample was prepared from a large quantity of flue dust by standard sampling techniques. The smelter dust, of course, varies in composition from day to day, depending on many variables, e.g., feed material, gas velocity and temperature, sampling point, etc.

is a general practice among the smelters, also poses a problem of circulating dust loads. It takes five recycling steps to treat most of the flue dust reintroduced in the smelting operation, Mackey and Bailey, 1978 (1), Figure 3. Also, each ton of flue dust that is retreated in the furnace decreases the amount of new concentrates that can be smelted.

In the past when the demand for arsenicals was high, the smelters found it economical to separate arsenic by first volatilizing it off from the flue dust and then condensing it in special chambers called kitchens. But demand for such arsenicals has diminished as a result of the toxicity generated in the soils where they were used and the subsequent regulations to control the use of these arsenicals. Since the economic incentive has been lost, the nonferrous smelters are faced with a dilemma. Continued recycle of the flue dust results in arsenic contaminated final products. Open storage in tailing ponds or landfill sites is an unacceptable means for disposal because of potential arsenic leaching into the ground-water and a very real financial loss resulting from the loss of valuable metals that are not recovered. To avoid this situation, alternate, as well as innovative, means are needed to convert arsenic into an environmentally safe and stable storable form.

SCOPE

The two year project results are summarized in this report. The study is divided into the following major parts: a study of



Number of Recycling Steps

(After Mackey and Bailey, 1978)

Figure 3. Relation between recycling and total input.

the dissolution characteristics of the starting flue dust in several aqueous environments; a study of several fixation techniques to produce a fixed form that is a safe storage product; and a study of the long term stability of the fixed products.

SECTION 2

CONCLUSIONS

The results of experimental leaching studies on the dissolution of arsenic from smelter flue dust wastes indicate that several conventional lixiviants can yield results sufficient to warrant leaching as an effective impurity rejection method dependent upon the specific chemical and mineralogical compositions of such materials.

Specific parameters of lixiviant composition, time, temperature, and liquid-to-solids ratio must be determined empirically for each individual flue dust in order to maximize arsenic extraction, achieve selectivity with respect to other heavy metal constituents, conserve chemical reagents, and mollify reaction conditions. No single combination of lixiviant composition and leaching conditions is considered optimum for a diversity of flue dust waste materials.

The arsenic content of sulfate-based leach liquors can be effectively recovered as a solid residue by coprecipitation with hydrated ferric oxide at mildly acidic solution pH. Residual arsenic concentration in solution can be reduced to well below one part per million when such precipitation is carried out in the presence of naturally occurring calcium phosphate (collophanite), although a reversion of arsenic solubility to approximately one part per million occurs when arsenic-bearing hydrated ferric oxide precipitates are equilibrated with pure water over periods of several months.

The use of particulate material to chemisorb arsenic from solutions does not appear to be a viable technique. Excessively large quantities of solid particulate would be required for successful removal of arsenic to desirable concentration levels. Therefore, large quantities of sludge material would have to be handled and stored.

The results of arsenic fixation in the flue dust via lime roasting to form calcium arsenate with subsequent treatment to further hinder arsenic release to an aqueous environment appears to be a viable dispersal technique. The arsenate dust material can be dissolved in molten slag or encapsulated in cements, concretes, or mortars. The most promising disposal technique appears to be dissolution in a slag matrix.

Clays have been shown to retain arsenic by adsorption mechanism. The form of arsenic being adsorbed plays a strong part in the retention. Chemically maintained disposal sites using clay beds for arsenic adsorption may be of some use. Cements and concretes show good arsenic retentions using low arsenic levels. At higher levels, from 3 percent arsenic and more, arsenic adversely affects the physical properties of cements and concrete. These properties were not the subject of any study in this report. Chemically, arsenic is retained because of the basic environment in the cements and concretes.

SECTION 3

RECOMMENDATIONS

The retention of arsenic compounds in a slag matrix has been successfully demonstrated. If the nonferrous smelters were to resort to this technique for arsenic disposal, a few small tests employing arsenic compounds introduction directly into the molten slag are needed. This will demonstrate not only the feasibility of the process but also make available a large quantity of arsenical slag for long-term leachability testing. It would answer the question whether the product is environmentally safe to be disposed of on land without any need for chemical and physical maintenance. It is also recommended to study possibilities of slagging arsenic directly into the furnace by making certain chemical changes in the furnace. Although to employ such a change which definitely would result in the changes in the furnace operational parameters, individual smelter interest and cooperation would be required.

The clays, particularly of the montmorinollite types, show a significant capacity for arsenic adsorption under the right environment, however, disposal of such arsenic laden clays in a site may yet have some problems. Arsenic adsorption and retention are dependent on a particular environment. Any environmental change may release arsenic at detrimental levels. It is recommended that further studies be made to determine the relationship between the different environments and arsenic retentions. Cements are capable of retaining arsenic at low levels. At the higher levels, arsenic detrimentally influences the cement properties. This is also true in the concrete case. It is of interest to mention here that the use of arsenical slag as a fill material in the concrete did not influence the structure as such although the slag as a fill material may have an influence on the mechanical properties of the concrete. Clays, cements, and concretes show good retentions of arsenic at low levels but their leachabilities should be determined on a larger scale to answer the question of stability.

SECTION 4

MATERIALS AND METHODS

EXTRACTION OF ARSENIC

Flue Dust Source Material

The raw flue dust source materials used in the present study were collected from a variety of western United States nonferrous smelting operations which treat sulfide ores and concentrates of copper, lead, and zinc. Since the primary objective of the present investigation is to study the behavior of arsenic contained in such materials, no documentation as to specific source is offered. All materials have, however, originated as dusts during the materials handling, drying, roasting, smelting, converting, or refining of such materials to produce a metallic product. In some instances, more than one dust sample was solicited from a single source.

Chemical Characteristics of Flue Dusts--

A total of nine raw flue dust samples were collected for study. Due to the preponderance of copper smelting plants treating arsenical materials in comparison to lead/zinc facilities, sample collecting effort was concentrated on assembling material from the various primary copper smelters. One sample was collected from a primary lead smelting facility. No samples were collected from any of several minor-metal producing operations nor were any materials knowingly collected from secondary treatment facilities including scrap-, slag-, or electrolytic refinery residue-treating processes.

Partial chemical analyses of the nine flue dust samples were made for four randomly-collected "grab" samples selected from each lot of preblended dust. Average elemental determinations were then tabulated and used to represent the composition of the entire lot (Table 2). A more elaborate sampling and analysis procedure was considered unnecessary for this study since all material examined was found to be extremely consistent with respect to composition and a deliberate attempt was made to restrict the number of analytical determinations required. The following brief tabulation illustrates the degree of consistency observed (Table 3).

TABLE 3. PRECISION OF CHEMICAL ANALYSIS

Constituent	First Determination,%	Second Determination,%	Third Determination,%	Fourth Determination,%
Arsenic	8.0	7.9	8.1	8.1
Copper	18.2	18.2	18.2	18.2
Iron	15.5	15.8	15.5	15.6
Zinc	5.7	5.9	5.8	5.8
Cadmium	0.20	0.20	0.20	0.20
Lead	3.6	3.6	3.6	3.6
Bismuth	0.37	0.39	0.38	0.37

TABLE 2. CHEMICAL ANALYSES OF RAW FLUE DUST SAMPLES

Constituent, %	SFD - A	SFD - B	SFD - C	SFD - D	SFD - E	SFD - F	SFD - G	SFD - H	SFD - I
Arsenic	8.0	20.0	29.4	3.8	10.7	0.20	3.4	2.7	3.4
Copper	18.2	4.76	3.91	10.6	0.21	19.8	4.55	27.7	23.2
Iron	15.6	6.1	1.43	10.4	0.72	17.5	5.0	23.8	15.8
Zinc	5.8	14.3	12.3	4.4	12.2	5.37	1.12	4.8	2.81
Cadmium	0.20	0.94	0.65	0.35	1.01	0.05	0.07	0.15	0.11
Lead	3.6	5.8	5.3	24.5	45.0	3.48	0.62	1.34	2.21
Bismuth	0.38	0.65	0.94	2.98	--	0.61	0.17	0.11	0.22
Antimony	0.36	0.63	1.26	0.21	4.24	0.07	0.07	0.36	0.09
Tin	0.48	0.75	1.60	1.68	0.92	0.28	--	--	--
Tellurium	0.22	0.27	1.69	0.12	--	0.14	0.04	0.13	0.05
Sulfur (as sulfate)	4.4	5.1	4.1	8.3	2.2	10.6	2.2	3.0	3.5
Sulfur (as sulfide)	4.9	4.9	3.8	2.3	0.4	0.6	0.7	8.5	16.9
Silver, oz/t	7.4	--	--	10.8	3.5	--	1.78	4.0	4.9

The chemical composition of the various dust materials examined indicates that a wide variety of feed materials are treated by industry. In addition to a variety of feed materials, each operating plant can be expected to utilize different extraction processes, equipment, and operating conditions with the result that no one dust product can be considered typical of the problem under study. The data presented in Table 2 illustrate that, dependent upon quantity, some nonferrous producers must cope with arsenic disposal problems which are several orders of magnitude greater than others. Virtually all producers generate and collect dust products which contain varying amounts of other elements which must be considered to contribute to the problem of dust retreatment/disposal from the standpoint of economic loss or environmental protection.

Volatile Constituents--

In most copper smelting processes, flue dust products contain large relative amounts of such elements as arsenic, zinc, cadmium, lead, bismuth, antimony, tin, and tellurium. Most of these elements are found to exist in flue dust in the form of oxides and sulfates. Their occurrence is largely brought about through volatilization of oxide, suboxide, sulfide, and, in some cases, elemental forms. Except in rare instances, such elements are true potential waste products. The ultimate chemical form of such elements is dictated by temperature and the chemical environment prevailing during transport, collection, and storage.

The dusts described in Table 2, except for SFD-H and SFD-I which are predominantly sulfidic, all show an essentially desulfurized condition in which the majority of the residual sulfur has been fully oxidized to sulfate indicating either generation or transport in a high temperature, oxidizing environment. The majority of these species have been formed by condensation or desublimation of vapors or as fumes.

Nonvolatile Constituents--

The elemental copper and iron, among others under certain circumstances, generally report to flue dust products as particulate material entrained by a moving gas phase. As a result, the particulate size of such constituents is generally larger and, hence, the relative amount of each reporting to the dust is normally quite small.

Mineralogical Characteristics of Flue Dusts--

Flue dust materials are generally difficult to characterize mineralogically due to several factors. Most importantly, several dozen chemical compounds are frequently present in such small amounts that X-ray diffraction techniques are all but useless. Major constituents are amenable to identification by diffraction analysis but, for the most part, petrographic microscopy applied to either bulk or physically segregated sample fractions must be resorted to for purposes of phase identification. Several of the flue dust samples described earlier in Table 3 were examined to illustrate the approximate distribution mineral species present in the dusts (Table 4).

TABLE 4. MINERALOGICAL ANALYSES OF RAW FLUE DUST SAMPLES

Constituent,vol %	SFD-A	SFD-B	SFD-F	SFD-I
$CuFeS_2$	5	4	13	9
Cu_2S	8	4	15	10
Cu_5FeS_4	3	2	5	3
CuS	1	1	Trace	1
Cu (element)	Trace	Trace	Trace	Trace
Cu_2O, CuO	14	3	4	7
$CuSO_4 \cdot xH_2O$	7	2	6	9
Fe_3O_4, FeO	13	2	24	17
Fe_2O_3, FeOOH	7	2	4	4
FeS, FeS_2	Trace	Trace	1	1
As_2O_3	11	16	4	6
ZnS	Trace	Trace	Trace	Trace
ZnO, $ZnSO_4 \cdot H_2O$	13	40	10	13
PbS	--	Trace	--	--
$PbSO_4$	1	11	2	3
SiO_2, Al_2O_3, etc	16	13	12	17

The data indicate the constituents such as copper and iron are distributed rather uniformly among sulfide mineral species present in the smelter feed, thermal decomposition products such as Cu_2S and CuS, and direct oxidation products. Copper sulfate, variously hydrated, is usually present in significant amounts and may be either a direct oxidation product or a result of the resulfation of copper oxides in SO_2/SO_3 atmospheres at moderate oxygen concentration and temperature. Virtually all simple sulfides of iron such as pyrite (FeS_2) and pyrrhotite (FeS) are found to be absent due to the oxidizing conditions under which smelter flue dusts are usually generated.

The minor elements, including arsenic, are frequently more difficult to characterize. For the dusts described in Table 5, arsenic can be positively identified as occurring in the form arsenic (III) oxide. It is difficult, however, to positively rule out the presence of other complex compounds of arsenic in spite of the fact that available techniques fail to disclose their presence. Lead and zinc are generally found to be present in flue dusts in the form of sulfates which is readily verified by solubility characteristics. Other minor elements are probably present in the form of oxides, basic sulfates, and the like although no direct evidence is available to support such a claim.

Particle Size of Flue Dust--

The fact that a substantial portion of smelter flue dust products are generated by fuming and gas-borne transport processes would naturally lead to the assumption that particle size distribution in such materials would be skewed towards very fine sizes. The dust samples described in Table 4 were characterized by standard screen analysis procedures with the result that particle size was found to be substantially minus 400 mesh (Table 5). With minor numerical differences, all four dust samples were found to be of essentially the same particle size distribution.

Methods of Chemical Analysis

All procedures for the chemical analysis of samples were adapted from either:

> Furman, N.H., et al, eds. Standard Methods of Chemical Analysis. 6th Ed., D. Van Nostrand Company, Inc., Princeton, New Jersey, 1962.

or,

> Taras, M.J., A.E. Greenberg, R.D. Hoak, and M.C. Rand, eds. Standard Methods for the Examination of Water and Wastewater. 13th Ed., American Public Health Association, New York, New York, 1971.

AMBIENT TEMPERATURE FIXATION

Starting Materials

The materials used in the low temperature arsenic fixation study are as follows: Arsenic flue dust obtained from a copper smelter, bentonite clay from Northeast Montana, Cottrell dust from a cement manufacturing plant, and phosphate rock from Southwest Montana.

Portions of bentonite clay and phosphate rock were crushed to 30 mesh. The crushed solids and a portion of the arsenic flue dust and Cottrell dust were individually mixed by rotation and

TABLE 5. SCREEN SIZE DISTRIBUTION OF RAW FLUE DUST SAMPLES

Tyler Mesh Size	Cumulative Percent Passing			
	SFD-A	SFD-B	SFD-F	SFD-I
65	88.2	91.8	99.3	89.3
100	87.4	90.7	99.2	88.0
150	86.7	90.0	99.0	87.1
200	85.7	89.3	97.3	86.1
270	85.1	89.0	94.7	84.8
325	84.1	88.7	88.7	82.9
400	83.3	88.6	84.9	81.4

shaking in large containers. Smaller portions, approximately 5 lbs., were sorted in plastic bags for use in the laboratory.

Each of the four solids were analyzed by a d.c. photographic emission spectrograph. The metals identified are those having a spectrum within the wavelength of 2000 A° to 4900 A°. In addition, a semi-quantitative analysis was performed via comparison of the spectra of various solid-graphite dilutions with that obtained from spec standards of 0.1, 0.01, 0.001, and 0.0001 weight percent of the metals. These qualitative and semi-qualitative data are illustrated in Table 6.

The four solids were analyzed for arsenic concentrations using the atomic absorption technique and are shown in Table 7.

TABLE 7. ARSENIC CONCENTRATION IN SOLIDS

Solid	Wt. % As	Solid	Wt. % As
As flue dust	16.24	Cottrell dust	0.40
Phosphate rock	0.74	Bentonite	0.25

Chemical Characteristics of the Starting Materials--

On the basis of the emission spectrographic and X-ray analysis, the phosphate rock contains a significant amount of fluoroapatite. Since the apatite is expected to serve as a medium for the absorption and adsorption of arsenic, this material is acceptable as an arsenic "getter", Mehta, 1977 (3).

TABLE 6. SEMI-QUANTITATIVE METAL CONCENTRATIONS IN SOLIDS (wt.%)

	PHOSPHATE ROCK	COTTRELL DUST	BENTONITE	FLUE DUST
Ag	.05	.005	-	.1
Al	>.1	.085	.08	> .1
As	-	-	-	> .1
Bi	.005	<.01	<<.01	> .1
Ca	> 1	>.1	.009	.08
Cd	.009	-	-	.08
Cr	.05	-	-	< .01
Cu	.095	.009	<.0001	> .1
Ga	.01	<.01	<.01	.09
Ge	-	-	-	.013
Hi	.09	<.01	<.01	.009
In	-	<.009	-	.080
Mg	>.1	>.1	>.1	>.1
Mn	<.01	.02	.01	<.01
Mo	-	.001	>.001	.08
Na	.02	.05	.009	.09
Pb	.005	.13	-	>.1
Si	.1	> 1	.1	>.1
Sb	.08	-	-	.05
Sn	.005	-	-	.09
Ti	.1	.1	.0009	.01
V	.05	-	-	.009
Zn	.065	.06	-	.1
P	> 1	-	-	-

The calcium in the Cottrell dust is distributed between calcite and calcium oxide. From earlier work on another project, Diebold, 1975 (5), the X-ray diffraction data on water leached Cottrell dust indicate that the majority of the calcium phase is calcite. Typical concentration of the Cottrell dust is as follows: 38 percent CaO, 2 percent MgO, 18 percent K_2O, 12 percent SiO_2, 3 percent Al_2O_3, 1 percent Fe_2O_3, 5 percent SO_3, and 19 percent LOI. Thus, the applicability of the Cottrell dust may depend upon an acidic media dissolving the calcite, thereby making the calcium available for arsenite and/or arsenate precipitation.

The X-ray diffraction data indicate that the bentonite contains a high percentage of montmorillonite. Since this clay mineral has been classified as a colloidolelectrolyte, it would appear that the bentonite would serve as an absorption and adsorption medium for the arsenic, Marshall and Krivbill, 1942 (4).

Each of the four solids were subjected to X-ray diffraction analysis. The results of this work are presented in Table 8. As in the metal concentration study, the X-ray data for the power plant ash are not presented at this time.

TABLE 8. X-RAY DIFFRACTION OF SOLIDS

Solid	Phases	
Phosphate rock	Fluoroapatite	$Ca_5F(PO_4)_3$
	Quartz	SiO_2
Cottrell dust	Calcite	$CaCO_3$
	Calcium oxide	CaO
Bentonite clay	Montmorillonite	$(OH)_4Si_8(Al_{3\cdot34}Mg_{0.56})O_{20}$
	Beidillite	$(OH)_4(Si_{6.34}\cdot Al_{1\cdot66})Al_{4.34}O_{20}$
Arsenic flue dust	Arsenolite	As_2O_3

Methods of Chemical Analysis

Early in this project a photographic quantitative emission spectrographic procedure was established for determining the arsenic concentration of the solid phases. This procedure, utilizing a d.c. arc, exhibited an accuracy of 3.6 percent of the amount present and an experimental precision of ±5.0 percent, expressed as relative standard deviation. The useful range was 0.6 to 60 percent arsenic and the detection limit of 0.06 percent, or 600 ppm As.

An atomic absorption procedure utilizing a nitrous oxide-acetylene flame was established for analyzing both high and low concentrations of arsenic in the aqueous solutions. For the high concentration range (i.e., 500 to 20 ppm), a linear calibration curve was obtained by aligning the burner head perpendicular to the line of light (λ = 193.7 nm) from the arsenic hollow cathode lamp. The linear range can be extended to 1000 ppm by making the flame more fuel-rich, thereby, decreasing the sensitivity but increasing the range of linearity. For the low concentration range, i.e., 20 ppm to 1 ppm, analysis was performed with the burner head parallel to the line of arsenic light. These calibration and analytical data were obtained by using the single-beam mode with background correction and recording the signal with a recorder at 50 mv full span.

The possible effect of pH and kind of anion were investigated by altering the pHs' of appropriate high and low concentration standards with an aqueous solution of NaOH followed by adjustment to specific pHs' with HCl and H_2SO_4 (Table 9).

T-1

TABLE 9. EFFECT OF ANION AND pH UPON As SIGNAL

Acid Used	pH	Recorded PPM As	Acid Used	pH	Recorded PPM As
200 ppm As Standard			20 ppm As Standard		
HCl	2.00	220	HCl	2.30	18.8
	3.75	199		3.12	18.2
	7.85	217		3.95	18.2
	8.72	205		5.55	16.7 * 18.4 ± .4
	9.45	221 212 ± 10 ppm			
H_2SO_4	2.60	218	H_2SO_4	2.40	22.3
	3.20	216		3.50	19.9
	8.22	217		4.75	20.0
	10.00	217 217 ± 1 ppm		8.4	17.2 * 20.7 ± 1.4

* Averages and standard deviations taken without considering the last high pH entry.

The effect of different oxidation states of arsenic upon the arsenic signal was investigated. Standard As (III) solutions were treated with calcium hypochlorite and potassium permanganate to oxidize the As (III) to As (V). A qualitative test for As (III) and As (V) indicated the presence of only As (V) in these oxidized arsenic solutions. No statistically significant difference in the As (III) signals and the As (V) signals were observed. Analysis of two month old standards, using a fresh set of standards, did not indicate any aging effect of the solution. The storage vessels were both polyethylene and pyrex.

Experiments were conducted to discern whether or not the matrix of the unknown solutions as compared to the synthetic standards had an effect. The unknown solutions were initially generated by leaching the arsenic flue dust with 1N H_2SO_4, 1N NaOH, and demineralized H_2O. Later in this study, the unknown solutions were those generated in the fixation experiments. Spikes of a high and low concentration standard were added to the appropriate unknown solution and the percent recovery recorded. These data are noted in Table 10.

TABLE 10. RECOVERY OF STANDARD ARSENIC SPIKES

Solution	Recovery, %
As flue dust - NaOH leach system	94.8 ± 10.1
As flue dust - H_2O leach system	103.6 ± 10.6
As flue dust - H_2SO_4 leach system	97.1 ± 0.6
Fixation liquids	106.5 ± 4.7

The AA procedure for aqueous solutions was extended to include solids. The solids phases were initially wetted with aqua regia and dissolved with hydrofluoric acid by heating in a teflon-lined acid digestion bomb at 105°C for 60 minutes. Upon cooling, boric acid was added to complex and free fluoride as a hydrofluroboric acid complex. The solutions were then diluted to volume and the AA analysis performed as indicated earlier for the aqueous solutions. The standard solutions were prepared in the same manner as the unknown solutions in the bombs. No arsenic loss was detected in the standards during the bomb digestion.

Effects of Variables--

The data presented above illustrate that the AA procedure utilizing a nitrous oxide flame is relatively free of interferrents present in the aqueous solutions generated during this study. The effect of pH, noted in Table 9, means that the pH of all samples should be adjusted to five prior to analysis. Although this operation would have an effect upon the precision, it is not considered to be significant due to the relatively small amount of concentrated H_2SO_4 used to adjust the pH. These studies indicate that there is not a statistically significant effect due to the presence of As (III) or As (V), $KMnO_4$, calcium hypochlorite, or acid anion.

SLAGS

The experimental work involved the use of various molten solvents for dissolution of arsenic containing forms. The molten solvents investigated are:

a) Slags: Copper Reverberatory Slags
Lead Blast Furnace Slags
Phosphorus By-Product Slags
Sodium Silicate Slags

b) Phosphorus containing rock

c) Montmorinollite and kaolinite clays

d) Mixtures of the above

The forms of arsenic being used in the dissolution studies are iron arsenates and calcium arsenates. These were prepared in the laboratory using arsenic acid (H_3AsO_4), arsenic pentoxide (As_2O_5), lime (CaO), hydrated lime [$Ca(OH)_2$], and ferric chloride ($FeCl_3$). The use of various arsenic, calcium, or iron sources was based on the availability of the chemical at the time only and there was no preference. These were used in their stoichiometric proportions, aided by an oxidizing agent such as hydrogen peroxide. The resulting arsenates were filtered, dried, and characterized as to their composition and form by chemical as well as X-ray diffraction analyses.

The formation of calcium arsenate was easily confirmed by the X-ray diffraction analysis although it is suspected that there may be some arsenites present in calcium arsenates. For iron arsenate, the compound identification by X-ray analysis was of no use as it did not show any particular pattern. This is true of a noncrystalline material. Iron arsenate was assumed to be present from the chemical analysis when it showed the arsenic content at about 38 percent. This is the amount of arsenic present in iron arsenate ($FeAsO_4$) when the compound is prepared stoichiometrically. Other techniques used to identify the compound were the determination of pentavalent arsenic and the heat treatment. The latter was used to drive off any structural water from the compound. For all practical purposes, the compound was termed as iron arsenate. This is a difficult choice for any research work but one has to make it considering that the iron arsenate as a reagent is very expensive and, also, that it is fast disappearing from the market as no replacements are being made.

Arsenates were used as starting materials mainly for their arsenic carrying ability, i.e., they have a low vapor pressure and will not boil out of the system before the slag becomes molten. Flue dust or arsenic oxide cannot be used directly because it will vaporize away from the system beore it has a chance to dissolve. The pyrometric cone equivalent of the laboratory prepared arsenates and other starting materials are presented in Tables 11 and 12 to illustrate the softening points of all starting materials. The chemical compositions of the various slags and starting materials are presented in Tables 13 and 14.

CLAYS

Montmorillonite and kaolinite clays were used in experimental work. For montmorillonite clay, bentonite was used as it closely approaches and resembles the former in composition.

TABLE 11. PYROMETRIC CONE EQUIVALENTS - AS RECEIVED MATERIALS

Cone Materials	Cone Value (2)	Cone Temperature (^{o}C)
Bentonite-M	8	1260
Bentonite-2	6	1230
Fly Ash	8	1260
Phosphorus Production By-product Slag	8	1260
Reverberatory Slag	3	1170
Lead Blast Furnace Slag	4	1190
Cement Dust	> 12	1335
Iron Arsenate Precipitate (1)		1000
Calcium Arsenate Precipitate (1)		1290
Phosphate Rock	> 12	1335

(1) Prepared in MRC Laboratory

(2) Heating rate approximately 150^{o}C/hr.

TABLE 12. PYROMETRIC CONE EQUIVALENTS - MIXTURES

Cone Materials (1)	Cone Value (2)	Cone Temperature (^{o}C)
Iron Arsenate-Bentonite	3	1170
Iron Arsenate-Bentonite (2)	< 01	< 1145
Iron Arsenate-Fly Ash	5	1205
Iron Arsenate-Phosphate Rock	6	1230
Iron Arsenate-Phosphorus Slag	6	1230
Iron Arsenate-Reverberatory Slag	6	1230
Iron Arsenate-Lead Blast Furnace Slag	2	1165
Iron Arsenate-Cement Dust	11	1325
Calcium Arsenate-Bentonite (m)	6	1230
Calcium Arsenate-Bentonite (2)	5	1205
Calcium Arsenate-Phosphorus Rock	6	1230
Calcium Arsenate-Phosphorus Slag	11	1325
Calcium Arsenate-Reverberatory Slag	8	1260
Calcium Arsenate-Cement Dust	> 12	1335
Calcium Arsenate-Fly Ash	8	1260
Calcium Arsenate-Lead Blast Furnace Slag	6	1190

(1) Mixtures of arsenate-matrix on a 1:1 ratio

(2) Heating rate approximately 150^{o}C/hr.

TABLE 13. SLAG COMPOSITIONS

	Lead Blast Furnace Slag %	Copper Reverberatory Slag %
Cu	0.3 - 1.0	0.50 - 0.7
Pb	0.1 - 0.2	--
Zn	2 - 2.5	2 - 4
SiO_2	25 - 30	35 - 40
CaO	20 - 35	6 - 7
FeO	33 - 35	40 - 45
MgO	2 - 2.5	--
S	2 - 3	0.5 - 1

TABLE 14. PHOSPHOROUS ROCK AND SLAG COMPOSITION

	Phosphorus Slag %	Phosphorus Rock %
SiO_2	17 - 21	8 - 15
CaO	38 - 45	20 - 35
FeO	0.1 - 0.6	1 - 1.5
Al_2O_3	1 - 2	1 - 3
P_2O_5	2 - 3	25 - 26

These two clays were chosen primarily for their exchange capacities.

The forms of arsenic used in this study were arsenic trioxide, iron arsenate, and calcium arsenate. Arsenic trioxide was of commercial grade, analyzing 95 percent as As_2O_3. Iron and calcium arsenates were prepared in the lab using the technique as described in the slag section. The composition of the starting clay is presented in Table 15.

TABLE 15. CLAY COMPOSITION

	Kaolinite, %	Montmorillonite, %
SiO_2	46.5	66.7
Al_2O_3	39.5	28.3
H_2O	14.0	5.0

CEMENT AND CONCRETES

Portland cement of Type 1, gravel, and sand were used in the experiments. These are all commercial materials and were obtained from a local business. Arsenic forms used were arsenic trioxide, calcium and iron arsenates, and arsenical slags. The arsenates were prepared as described in the slag section. Arsenic trioxide was of commercial grade as in the clay section. Arsenical slags were originally prepared for the test work on arsenic dissolution in the smelter slag. These were used as filling material for concrete making.

LEACHING TESTS

The effectiveness of any fixation scheme depends on whether it has been successful in preventing the migration of the pollutant to the environment. Since the fixed product is to be disposed of on the land, primary concern is the movement of the pollutant to the hydrosphere. Whenever water comes into contact with a solid material, potential for leaching of the pollutants exists. The rate of leaching for a solid material or for the chemical species that exist in the solid material can be measured in the laboratory by various leaching tests. These tests help in predicting the scale of pollutant movement into an aqueous medium. Several testing procedures and equipments are available for this purpose; of these, only two were used for the project. These were the shake test and the column test. The factors of importance in performing either of these tests were the materials of construction for the test, specification for sampling, and the procedures for the leaching tests.

Shake Test

In a shake test, a solid is agitated with an element in order to generate a leachate. Conditions relating to the site specific parameters can be applied. The test is relatively simple, rapid, and inexpensive. Although it defines, in most cases, a worst case analysis, it provides data in terms of the concentration of species in the leachate. The actual field environmental factors that control leaching and the factors within the shake test are hard to relate. This is just a worst case analysis providing data on the maximum rate of leaching of the pollutants in terms of concentrations.

For the shake test used in this project, polyethylene plastic containers were used as leaching vessels. Distilled-deionized water equilibrated with room air was used as the eluant in all but one test. Controlling variables were defined as the pH of the water, temperatures, solid to liquid ratio, test duration, and the particle size. In most of the cases, the system was allowed to take its course regarding control of the pH; only in a few cases was any attempt made to control the pH.

The procedure for sampling for arsenic after a shake test was to measure the pH of the leachate, pipet two ml of the leachate, and replace it with two ml of distilled-deionized water. The leachate was then filtered through a 0.45 micron filter and analyzed.

Column Test

In a column test, a material to be leached is placed in a specially prepared column and eluted with a solvent. Conditions relating to site specific parameters could be applied. The test is inexpensive and would be performed with commonly available equipment. When carefully designed and run, this test could provide data which would show the rate of pollutant release to the environment.

The column tests used in this project were of two kinds; indoor and outdoor.

Indoor Test--

The columns were made of 8 inches of 1.5 in. diameter polyethylene plastic. The top of the column was capped with a two-holed rubber stopper. One hole was used as an inlet for the eluant. The second hole was left open for air to interact with the eluant. The sample was placed on glass wool resting on top of a perforated disc. The bottom of the column was constructed to collect the leachate and to direct it to the pump by a plastic tubing. Eluant flow was maintained at a specified rate (4 ml per min in our case) by a peristaltic pump. A glass tee was provided in the tubing to serve as a sampling port. The arrangement is shown in Figure 4.

Outdoor Test--

This test was designed to reflect some of the parameters of a field test cell. This is a large column installed outside in a field and exposed to field conditions in order to generate a leachate. The columns were four inches in diameter and eight inches long. The top of each column was open. The bottom end was fitted with a perforated disc and jointed with a funnel to direct the flow to a container. All materials were made of plastic. Glass wool was spread on the disc and the sample placed on top of it. The columns were left in the field until enough precipitation had fallen for a sample to be collected.

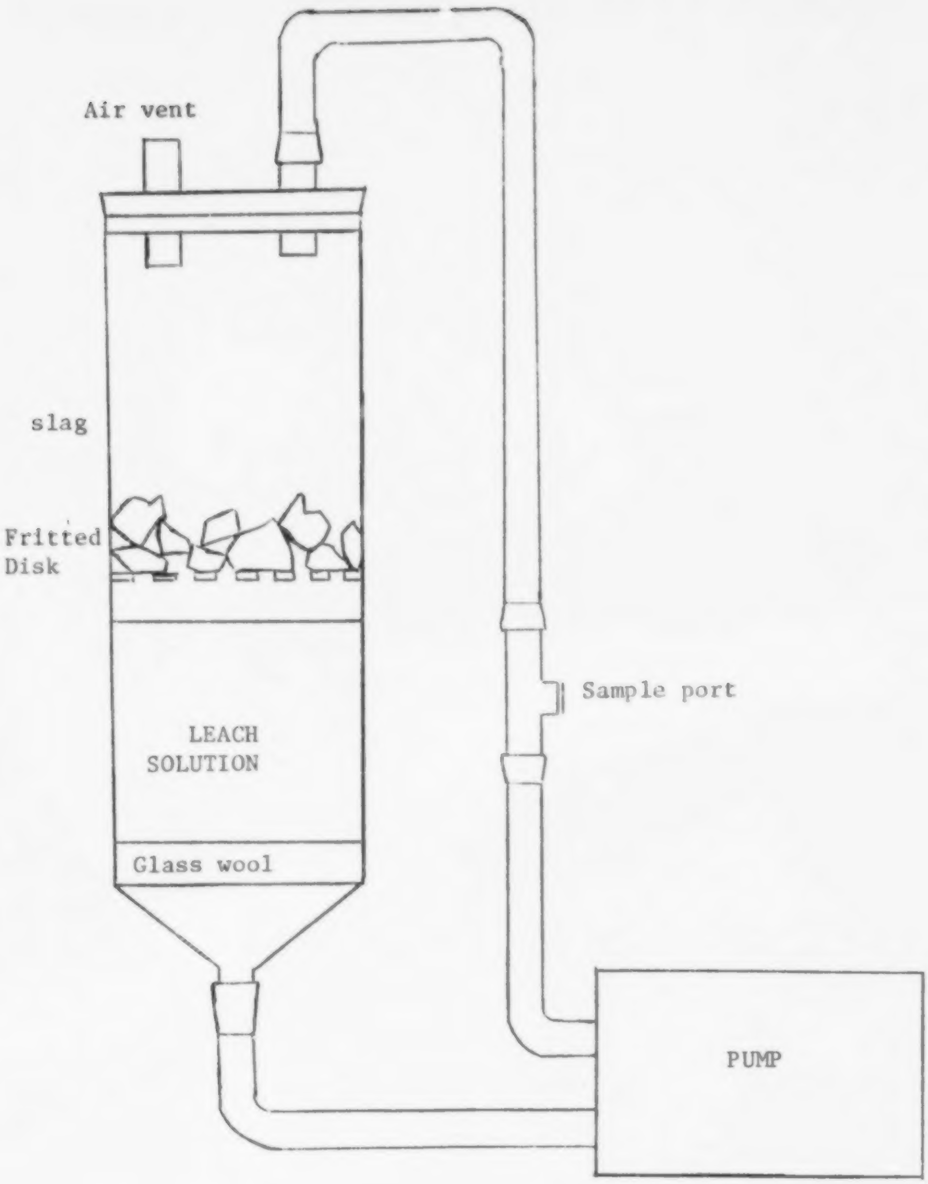


Figure 4. Column leach.

Chemical and Other Properties--

All the samples were analyzed for initial arsenic concentration in the fixed products and leach waters. pH values were taken for most of the leachates generated from the shake as well as column leach tests. Any other parameters for chemical properties were determined when the need existed.

Methods for Chemical Analysis

All procedures for chemical analysis were performed using the guidelines given in either:

> Furman, N.H., et al., Eds. Standard Methods of Chemical Analysis. 6th Ed., D. Van Nostrand Company, Inc., Princeton, New Jersey, 1962.

or,

> Methods of Chemical Analysis, Anoconda Company, Tucson, Arizona. Personal Communications, A. Mehta, 1976.

or,

> Standard Methods for the Examination of Water and Wastewater. 14th Ed., American Public Health Association. A.W.W.A., and W.P.C.F., Washington, D.C., 1975.

In case of arsenic determination by atomic absorption spectrophotometry, all samples were first screened to determine the relative concentration of arsenic by flame atomic absorption. If the concentration was lower than required for detection by flame, a heated graphite atomizer unit was used.

SECTION 5

EXPERIMENTAL PROCEDURES

EXTRACTION OF ARSENIC

The present investigation of hydrometallurgical techniques for the control of smelter arsenic flue dust wastes was implemented in the form of a screening program to assess the efficacy of a number of conventional lixiviants in regard to the dissolution of arsenic from a collection of different flue dust materials. Standardized leach and precipitation techniques were not used.

Leach tests were performed using a variety of simple and compound lixiviants prepared from reagent grade chemicals and distilled water. Most solutions used as leachants were standardized prior to use by a combination of chemical analysis and pH measurement. Except where specifically noted in the subsequent discussion, all leach tests were performed at 5 percent solids by weight to avoid saturation with respect to any potentially soluble species.

Control of solution pH was effected by use of a Corning Model 12 pH meter. Temperature control was achieved by means of thermostated hot plates or constant temperature baths to within an accuracy of ±3°C. Agitation was variously provided by means of magnetic stirring bars or teflon motor-driven stirrers. All leaching was performed in Pyrex laboratory ware. Collected samples of pulp were immediately separated by vacuum filtration and prepared for chemical analysis.

AMBIENT TEMPERATURE FIXATION

The fixation studies involved investigation of the arsenic sorption capability of the three solids, phosphate rock, bentonite, and Cottrell dust. The following arsenic media were used:

1. Solutions previously generated by leaching As flue dust with 1N H_2SO_4, 1N NaOH, and H_2O
2. Standard As (III) aqueous solutions
3. Standard As (V) aqueous solutions
4. Solutions of As flue dust in 1N H_2SO_4, or in 1N NaOH

In all but the As flue dust leachate solutions, two experimental procedures were utilized. One was the simple mixing of one of three solids with 50 ml of the arsenic media for 24 hours followed by filtering of the resulting solution through a 0.45 filter and its analysis via AA. This procedure was used with all four of the arsenic media. The second experimental procedure, which was used with all but the As flue dust leachate solutions, consisted of a two-hour mix of one of the three solids with 50 ml of the arsenic media followed by an approximate 24 hour 85°C drying step. This residue was then mixed with 50 ml of demineralized water for two hours, filtered through a 0.45 filter and, finally, the As concentration in the solution determined via AA. These experimental procedures are shown in Figure 5.

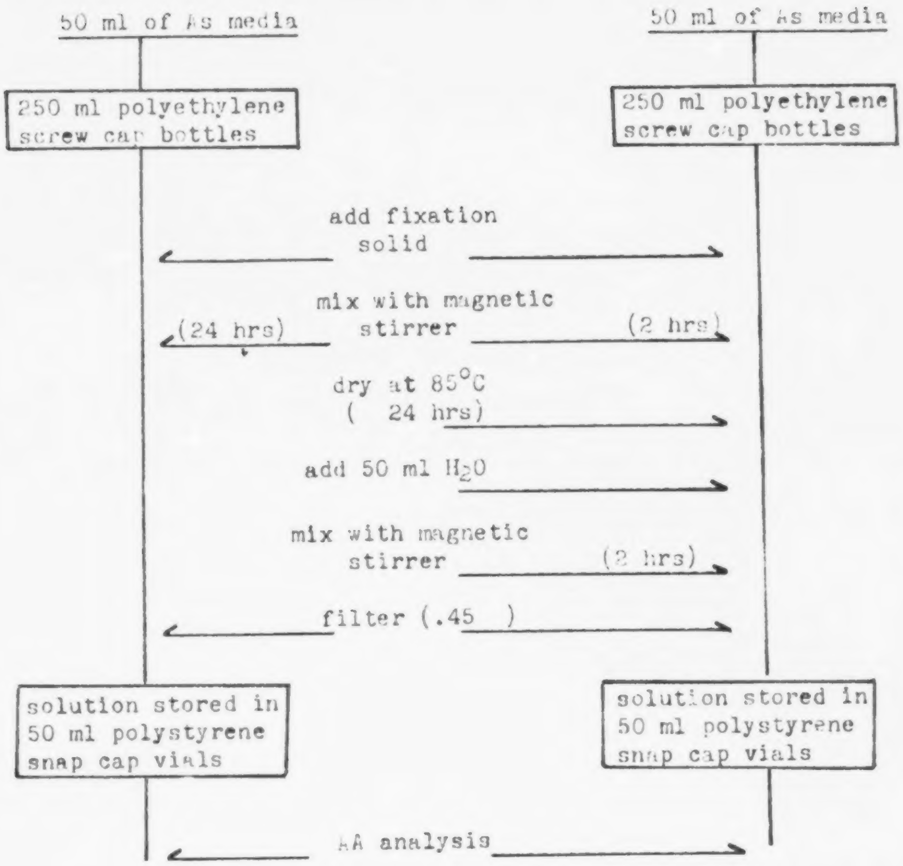

50 ml of As media
50 ml of As media
250 ml polyethylene screw cap bottles
250 ml polyethylene screw cap bottles
add fixation solid
mix with magnetic stirrer
(24 hrs)
(2 hrs)
dry at 85°C (24 hrs)
add 50 ml H2O
mix with magnetic stirrer
(2 hrs)
filter (.45)
solution stored in 50 ml polystyrene snap cap vials
solution stored in 50 ml polystyrene snap cap vials
AA analysis

Figure 5. Fixation studies - experimental modes.

In each of the first three fixation media, 5 grams of one of the three solids was used. In the fourth media, i.e., the acidic and basic aqueous suspensions of As flue dust, 1,2,4, and 6 gram additions of each of the three solids were used. Prior to AA analysis, the pH of each solution resulting from the fixation tests was checked with a pH paper and the pH adjusted to five or lower with concentrated H_2SO_4. Each fixation test was performed in duplicate, and the results calculated as the ratio of the mass of arsenic in solution to mass of solid versus the decrease in arsenic concentration in solution due to fixation.

ELEVATED TEMPERATURE FIXATION

Slag Systems

Retention of arsenic in a glass matrix has been studied as a possible chemical fixation route for arsenic. Experiments with the glass matrix were restricted to the slag systems as they approach and approximate glasses in compositions. Slag is a daily waste by-product of the smelting operations so it would be readily available for arsenic incorporation.

Fusion Testing--

The experimental procedure used for preparation of the arsenic containing slag was as follows: The solid arsenate was weighed in the desired proportion and added to a fireclay crucible. The material or a mixture of the materials to be used as the solvent was added to the crucible in solid form. The crucible was then placed in an electric muffle furnace at the desired temperature. Furnace temperature was controlled by a proportioning-type temperature controller to within an accuracy of ±5°C. Furnace atmosphere was not controlled and was assumed to be slightly of oxidizing nature. The samples were melted, removed, and poured into sample recovery pans. They were allowed to cool in air.

Data were collected on time and temperature of exposure. Qualifying notes were made on ease of pouring (fluidity), segregation, and reaction with the sample crucible.

Leach Testing--

Two types of leach tests were used: shake test and column test. The column test was divided into indoor and outdoor test.

Shake test--

The fixed products were leached using a shaker test. Experimental procedure was to use a solid to liquid ratio at 1:100. Sizes of the solids chosen were 8 mesh and -80 mesh. An appropriate portion of the solids was weighed out in 500 ml polyethylene bottles with screw caps. Distilled water in contact with room air was then added to produce S/L ratio of 1:100. Initial pH was measured using an Orion pH meter model 601A. The bottles were mounted in table top Burrell side-arm shaker units and shaken for one hour. pH was again measured and two ml of the leach solution were pipetted out for arsenic analysis. Two ml of distilled water were then added to the bottles to bring back the

S/L ratio to its original value. Leach solution samples were collected on a time interval basis repeating the same procedure.

No attempt was made to control the pH on a majority of the samples although a few leaching tests were performed using controlled pH's and different S/L ratios.

Column test--

Indoor test--Two slags made with calcium arsenate in a copper smelter waste slag, with initial arsenic concentration of 15.7 percent, were leach tested for arsenic release. Number 1 slag was placed on a plastic screen disc jointed in the middle of the leaching column (Figure 4). This arrangement lets the water trickle down the slag at a specified rate. Slag remains wet constantly but is not immersed in the water all the time. Number 2 slag was placed in the bottom of the leaching column so as to have it immersed in water constantly.

Slags 1 and 2 had the same S/L ratio of 1:1 but the first slag was 1/4 in. in size and the second slag was 1/2 in. in size. A third slag was prepared with five percent initial arsenic and was leached in a column in the same arrangement as Slag 1. The slag size was 1/4 in. and was leached with 1:10 solid to liquid ratio.

Outdoor test--Seven outdoor leach tests were started on arsenical slags. Of these seven, the first two were blank slags from a copper smelter and a lead smelter. Slag Samples 3 and 4 were made by fusing iron arsenate with lead smelter slag and copper smelter slag respectively. Samples 5 and 6 were prepared by fusing calcium arsenate with copper smelter slag and lead smelter slag respectively. Sample 7 contained no slag, but was used as a blank for environmental arsenic.

These leach columns, with the slags, were placed outdoors in a field. Sampling for arsenic was begun after enough precipitation had fallen.

Clays

Pelletization of arsenic compounds in different matrices and the subsequent treatment for arsenic fixation was the concept utilized here. The concept is one of chemical stabilization and physical entrapment resulting in a stable and storable form of arsenic. The approach was to physically impound the arsenic compounds in a clay matrix. The mixtures were formed into pellets, then roasted to give dense and physically strong pellets.

Pellet Preparation--

Arsenic compounds and clays and, in some cases, arsenic compounds and other industrial waste products were mixed in 25, 50, and 75 percent weight ratios. In each case, one gram of the mixture was placed in the die (1/2 in. diameter). The mixture was pressed with a two ton/in.^{2} pressure. Resulting pellets were removed, thermally treated, and subjected to leach tests.

In one particular case, arsenic compounds were mixed with different quantities of glazing material, which is mainly composed of silica, feldspars, lime, and fluxing agents, such as sodium and lead. The mixture was then placed in the die and pressed with a two ton/in.^{2} pressure. No water was added in any of the pressure procedures.

Sintering--

The pellets were sintered to drive off any volatile arsenic on the surface of the pellets. An electric tube furnace with a temperature controller was used. The pellets were sintered at 1000°C for 15 minutes. They were taken out and cooled after sintering.

Firing--

The pellets were then fired at 1000°C for 15 minutes to set the ceramic bonding.

Leaching--

Individual pellets were placed in plastic bottles. Distilled water in contact with air was poured into the bottles to give a solid:liquid ratio of 1:100. The bottles were put on the shaking machines and shaken for one hour after which the pH readings were taken and two ml were pipetted out for analysis. Two ml of distilled water were then poured back to return the S:L ratio to its original value. This procedure was repeated after 96 hours of continuous shaking. The pellets were left in the leach bottles for future testing.

Cements and Concretes

Casting--

Arsenic compounds were mixed in different proportions with the cements. In some cases mortar mix instead of the cements was used. Proportions used were 90 percent cement, 75 percent cement, 50 percent cement, and 25 percent cement; the rest of the sample was arsenic compounds. In one case, the proportioned weights of the mixtures were roasted at 200°, 400°, and 600°C before casting. In another case, the materials were mixed, cured, and roasted at 200°, 400°, and 600°C. In still another case, these materials were cast without any roast treatments.

The cement mixtures were cast in plastic ice cube trays to give uniform arsenic-cement samples of approximately one cubic inch size. Concrete blocks were cast in plastic cylinders of 4 inches diameter and 8 inches long. Along with gravel, arsenical slag was used as a filling material. Exact compositions and arsenic contents of the concretes appear in the section on Results and Discussion.

Curing--

The cement and concrete mixtures were cured for one week after which samples were taken for arsenic analysis and leach tests. One set was roasted before leach testing. Qualifying notes were made on the resulting cement structures.

Leaching--

The cast cubes of arsenic cement mixtures were leach-tested for arsenic release using a shaker test. The procedure is the same as described for the slag section.

Other Mixtures--

Flue dust-cement mixtures were also tried instead of the arsenic compounds. Procedures followed for mixing, curing, and leaching were the same as described above.

SECTION 6

RESULTS AND DISCUSSION

FLUE DUST LEACHING EXPERIMENTS

Mineralogical examination of several of the flue dust samples examined in the present study revealed the presence of substantial quantities of discrete arsenic (III) oxide which is known to be quite soluble in water. Simple water leaching of flue dust, however, fails to solubilize all of the contained arsenic. In order not to generate a multitude of waste disposal problems from what is initially a single arsenic containing source, a wide variety of other lixiviants was investigated in an attempt to identify a nearly-universal solvent for all of the arsenic-bearing chemical compounds present in the smelter flue dust samples studied.

The use of any chemical reagent for arsenic dissolution will understandably increase the cost of a potential arsenic extraction and recovery process. However, the advantages to be realized through confining arsenic to a single phase should more than offset any penalties resulting directly from the use of common leaching agents.

Leaching with Alkaline Ammoniacal Solutions

A series of leach tests was performed with two of the flue dust samples described in Table 2, SFD-C and SFD-H, utilizing an oxygenated ammoniacal-ammonium sulfate leaching agent at elevated temperatures. Dust SFD-C is a low-copper, high-arsenic containing dust of low sulfur content which is nearly equally divided between sulfide and sulfate. Dust SFD-H, however, represents a dust of opposite characteristics in which the copper content far exceeds the arsenic content. The sulfur content of SFD-H is also much higher than in SFD-C and is predominantly sulfidic in character.

All leach tests were performed using a naturally alkaline lixiviant containing sulfur as ammonium sulfate at a concentration of 2.38 gram-moles per liter and aqueous ammonia at various concentrations. Gaseous oxygen was sparged continuously on demand against a regulated overhead pressure. Temperature was regulated by means of steam-fed internal coils and external, insulated jackets. All tests were performed at 10 percent solids pulp density in closed agitated stainless steel leach reactors. Samples were withdrawn at time intervals by means of closed sample receivers, cooled, filtered, and prepared for analysis.

A total of four leach tests was performed using flue dust sample SFD-C. Samples of the leach pulp were collected at approximately one hour intervals, analyzed, and the results summarized (Tables 16, 17, 18, and 19). Arsenic extraction was found to be nearly complete under all conditions examined. Approximately 90 percent of the arsenic content of dust SFD-C was dissolved within the initial 5 to 10 minutes of leaching with no significant improvement noted as leach time was increased to 4 hours. Arsenic

TABLE 16. AMMONIACAL LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Leach Conditions:
Temperature - 50°C
Pressure - 0.422 kg/cm^2 (6 psig)
Initial free ammonia concentration - 4.0 percent

Sample Time, Hr.	Sample Product	Analysis, % or gpl							Distribution, %						
		As	Cu	Zn	Cd	Pb	Bi	Sb	As	Cu	Zn	Cd	Pb	Bi	Sb
0.1	Solution	24.5	3.84	23.6	0.81	<0.001	<0.001	0.08	88.6	66.6	95.8	77.4	--	--	10.7
	Residue	12.8	7.2	4.02	0.95	26.1	3.76	3.06	11.4	33.4	4.2	22.6	100	100	89.3
0.4	Solution	19.8	3.86	20.6	0.80	<0.001	<0.001	0.11	86.2	72.0	95.0	73.4	--	--	13.8
	Residue	13.9	6.2	4.44	1.2	27.3	3.96	3.22	13.8	28.0	5.0	26.6	100	100	86.2
1.0	Solution	19.6	4.40	22.4	0.81	<0.001	<0.001	0.12	88.0	81.2	96.0	76.3	--	--	16.6
	Residue	13.6	4.76	4.38	1.2	28.4	4.0	3.22	12.0	18.8	4.0	23.7	100	100	83.4
2.0	Solution	23.7	4.60	23.0	0.80	<0.001	<0.001	0.11	86.5	82.2	95.6	72.9	--	--	13.5
	Residue	15.9	4.14	4.42	1.25	28.4	4.16	3.28	13.5	17.8	4.4	27.1	100	100	86.5
3.0	Solution	24.3	5.14	22.4	0.92	<0.001	<0.001	0.12	86.9	85.0	95.6	81.1	--	--	14.1
	Residue	15.7	3.76	4.34	0.89	28.0	3.80	3.30	13.1	15.0	4.4	18.9	100	100	85.9

TABLE 17. AMMONIACAL LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Leach Conditions:
Temperature : 75^oC
Pressure - 0.422 kg/cm^2 (6 psig)
Initial free ammonia concentration - 4.0 percent

Sample Time, Hr.	Sample Product	Analysis, % or gpl							Distribution, %						
		As	Cu	Zn	Cd	Pb	Bi	Sb	As	Cu	Zn	Cd	Pb	Bi	Sb
0.1	Solution	24.7	3.66	23.0	0.77	0.012	<0.001	0.12	93.2	79.3	98.4	88.6	0.3	--	21.9
	Residue	14.3	7.2	4.30	0.80	30.5	5.04	3.05	6.8	20.7	1.6	11.4	99.7	100	78.1
0.5	Solution	24.1	4.00	22.6	0.75	<0.001	<0.001	0.12	94.6	87.6	97.8	87.0	0.2	--	24.7
	Residue	11.6	4.62	4.21	0.98	29.5	6.16	2.92	5.4	12.4	2.2	13.0	99.8	100	75.3
1.0	Solution	23.8	4.22	22.8	0.66	0.042	<0.001	0.13	93.6	87.7	97.9	85.6	1.2	--	27.4
	Residue	14.6	5.12	4.35	1.08	32.4	5.80	2.84	6.4	12.3	2.1	14.4	98.8	100	72.6
2.0	Solution	20.8	3.84	16.6	0.65	0.12	0.036	0.33	94.8	89.8	97.6	86.2	4.1	5.9	57.4
	Residue	13.1	4.32	4.87	1.13	30.7	5.10	2.20	5.2	10.2	2.4	13.8	95.9	94.1	42.6
3.0	Solution	18.8	4.24	15.2	0.66	0.164	0.036	0.49	87.4	88.3	88.6	74.9	4.1	3.5	66.3
	Residue	16.2	2.86	12.3	1.14	22.3	4.60	1.14	12.6	11.7	11.4	25.1	95.9	96.5	33.7
4.0	Solution	18.7	4.20	15.6	0.66	0.238	<0.001	0.54	95.5	94.0	97.8	87.2	8.6	5.9	71.3
	Residue	12.5	3.02	5.30	1.20	32.3	5.52	2.10	4.5	6.0	2.2	12.8	91.4	94.1	28.7

TABLE 18. AMMONIACAL LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Leach Conditions:
Temperature - 50°C
Pressure - 1.055 kg/cm^2 (15 psig)
Initial free ammonia concentration - 8.0 percent

Sample Time, Hr.	Sample Product	Analysis, % or gpl							Distribution, %						
		As	Cu	Zn	Cd	Pb	Bi	Sb	As	Cu	Zn	Cd	Pb	Bi	Sb
0.1	Solution	28.5	3.96	22.4	0.83	0.034	0.012	0.15	91.0	76.6	95.5	89.5	0.6	1.0	20.3
	Residue	12.8	5.38	4.62	0.43	29.8	4.96	3.37	9.0	23.4	4.5	10.5	99.4	99.0	79.7
0.5	Solution	26.6	4.50	21.8	--	--	--	--	90.2	82.3	95.5	--	--	--	--
	Residue	13.5	4.39	4.62	--	--	--	--	9.8	17.7	4.5	--	--	--	--
1.0	Solution	25.0	4.60	22.0	0.82	0.040	0.006	0.15	90.0	85.1	96.0	91.0	0.7	0.6	20.0
	Residue	14.0	3.92	4.44	0.39	31.3	4.92	3.34	10.0	14.9	4.0	9.0	99.3	99.4	80.0
2.0	Solution	14.7	5.24	22.6	--	--	--	--	85.3	86.8	95.9	--	--	--	--
	Residue	13.0	3.60	4.55	--	--	--	--	14.7	13.2	4.1	--	--	--	--
3.0	Solution	26.2	5.20	21.8	--	--	--	--	90.2	88.6	96.0	--	--	--	--
	Residue	14.1	3.18	4.32	--	--	--	--	9.8	11.4	4.0	--	--	--	--
4.0	Solution	27.1	4.40	22.0	0.84	0.052	0.012	0.15	88.9	86.8	95.7	92.0	1.0	1.0	21.2
	Residue	15.4	2.95	4.34	0.32	29.3	4.84	3.13	11.1	13.2	4.3	8.0	99.0	99.0	78.8

TABLE 19. AMMONIACAL LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Leach Conditions:
Temperature - 75°C
Pressure - 1.055 kg/cm^2 (15 psig)
Initial free ammonia concentration - 8.0 percent

Sample Time, Hr.	Sample Product	Analysis, % or gpl							Distribution, %						
		As	Cu	Zn	Cd	Pb	Bi	Sb	As	Cu	Zn	Cd	Pb	Bi	Sb
0.1	Solution	23.5	4.16	23.4	0.78	0.018	<0.001	0.17	90.4	86.9	95.4	86.1	0.2	--	28.3
	Residue	11.1	2.71	4.85	0.54	31.0	5.0	2.15	9.6	13.1	4.6	13.9	99.8	100	71.7
0.5	Solution	26.2	4.32	22.8	--	--	--	--	89.3	86.8	95.8	--	--	--	--
	Residue	14.5	2.89	4.42	--	--	--	--	10.7	13.2	4.2	--	--	--	--
1.0	Solution	26.3	4.28	23.2	0.81	0.001	0.012	0.19	88.2	84.4	95.7	88.6	--	1.2	23.5
	Residue	15.6	3.40	4.50	0.45	27.7	4.24	2.94	11.8	15.6	4.3	11.4	100	98.8	76.5
2.0	Solution	26.8	4.28	22.6	--	--	--	--	89.6	84.1	95.8	--	--	--	--
	Residue	15.2	3.75	4.61	--	--	--	--	10.4	15.9	4.2	--	--	--	--
3.0	Solution	28.6	4.54	22.2	--	--	--	--	90.1	84.2	95.8	--	--	--	--
	Residue	15.0	4.09	4.65	--	--	--	--	9.9	15.8	4.2	--	--	--	--
4.0	Solution	28.2	5.06	22.4	0.82	0.50	0.13	0.56	91.2	85.6	96.5	90.9	9.3	13.9	51.1
	Residue	15.1	4.72	4.49	0.45	27.1	4.56	3.07	8.2	14.4	3.5	9.1	90.7	86.1	48.9

solubility was also found to be independent of initial free ammonia concentration and oxygen overpressure. The latter variable would be expected to exert an influence of arsenic extraction only in the event that significant amounts of arsenic were present as residual sulfides. Increased temperature was found to have a slight but favorable influence on ultimate arsenic extraction but primarily at the lower free ammonia concentration.

The data in Tables 16 through 19 indicate that together with arsenic, a number of other flue dust components dissolve to a greater or lesser extent as well. Substantially all of the copper, zinc, and cadmium are also extracted more or less completely. In addition, a significant proportion of the antimony content is solubilized under all conditions examined and lead solubility begins to take effect at higher temperatures and longer times.

The leaching behavior of flue dust sample SFD-H in ammoniacal ammonium sulfate solutions was briefly examined under essentially the same conditions as those used for dust SFD-C but with less favorable results (Tables 20 and 21). The more sulfidic dust SFD-H showed significantly lower solubility characteristics with respect to arsenic, copper, and zinc, but greatly increased solubility of lead. As before, the effects of temperature and oxygen overpressure were minimal.

Leach data collected for ammoniacal solutions indicate that a significant fraction of the arsenic content of both dusts tested is immediately soluble under all conditions. This portion of the arsenic content is undoubtedly arsenic (III) oxide since leach residues, even when high in arsenic, fail to exhibit X-ray

TABLE 20. AMMONIACAL LEACH RESULTS FOR FLUE DUST SAMPLE SFD - H

Leach Conditions:
Temperature - 50^{o}C
Pressure - 0.422 kg/cm^2 (6 psig)
Initial free ammonia concentration - 6.0 percent

Sample Time, Hr.	Sample Product	Analysis, % or gpl				Distribution, %			
		As	Cu	Zn	Pb	As	Cu	Zn	Pb
0.1	Solution	1.5	14.0	7.60	0.24	43.7	44.0	69.0	14.1
	Residue	2.4	21.2	4.06	1.70	56.3	56.0	31.0	85.9
0.5	Solution	1.5	15.5	7.42	0.32	49.7	52.7	70.3	21.6
	Residue	2.1	18.6	4.18	1.57	50.3	47.3	29.7	78.4
1.0	Solution	1.6	17.0	7.66	0.46	51.7	59.2	71.7	29.3
	Residue	2.3	16.4	4.25	1.56	48.3	40.8	28.3	70.7
2.0	Solution	1.6	18.4	7.69	0.57	53.4	65.1	72.5	35.9
	Residue	2.2	14.8	4.34	1.45	46.6	34.9	27.5	64.1
3.0	Solution	1.6	19.5	7.76	0.62	62.9	68.2	73.0	41.3
	Residue	2.4	13.8	4.39	1.35	37.1	31.8	27.0	58.7
4.0	Solution	--	20.5	7.38	0.63	--	72.4	71.8	41.9
	Residue	--	11.9	4.44	1.41	--	27.6	28.2	58.1

TABLE 21. AMMONIACAL LEACH RESULTS FOR FLUE DUST SAMPLE SFD - H

Leach Conditions:
Temperature - 75°C
Pressure - 0.422 kg/cm^2 (6 psig)
Initial free ammonia concentration - 6.0 percent

Sample Time, Hr.	Sample Product	Analysis, % or gpl				Distribution, %			
		As	Cu	Zn	Pb	As	Cu	Zn	Pb
0.1	Solution	1.3	14.0	7.38	0.41	44.9	46.8	70.0	28.6
	Residue	2.0	19.2	3.82	1.26	55.1	53.2	30.0	71.4
0.5	Solution	1.7	17.5	7.08	0.54	46.6	58.1	69.6	38.5
	Residue	2.0	16.4	4.02	1.14	53.4	41.9	30.4	61.5
1.0	Solution	1.3	19.6	7.26	0.56	45.6	63.1	71.5	42.3
	Residue	2.3	16.0	4.05	1.17	54.4	36.9	28.5	57.7
2.0	Solution	1.2	22.2	7.36	0.51	42.8	72.4	72.4	36.9
	Residue	2.4	12.2	4.04	1.28	57.2	27.6	27.6	63.1
3.0	Solution	1.5	23.5	8.06	0.48	50.6	74.3	74.6	34.7
	Residue	2.2	12.0	4.03	1.36	49.4	25.7	25.4	65.3
4.0	Solution	1.2	24.1	7.80	0.44	41.7	76.5	73.7	32.0
	Residue	2.6	11.0	4.12	1.41	58.3	23.5	26.3	68.0

diffraction patterns for this compound although patterns have been obtained with the dusts prior to leaching. The balance of the arsenic is very slowly solubilized at greatly increased leach times indicating a rate controlled reaction. Perhaps the most discouraging information obtained from the ammoniacal leach tests was that solid-liquid separation characteristics of the leach pulps was uniformly poor. Flocculation and settling characteristics could be improved to some degree if lead solubility was kept to very low levels (less than about 0.1 gram per liter). The best results obtained however, remained poor from a practical viewpoint.

Leaching with Caustic Solutions

Solutions of sodium hydroxide are generally known to be excellent solvents for arsenic (III) oxide. To investigate this fact experimentally, several leach tests were performed using the flue dust sample SFD-B. Sodium hydroxide concentrations of from 0.5 to 5.0 molar were used at various temperatures up to 90°C for varying lengths of time.

Arsenic leach extraction varied from a low of 10 percent to a high of about 90 percent. No particular trends were observed as functions of test conditions however, and no discussions of leach results are offered due to their unexplainable erratic values.

The observation made in the above tests that significant extraction of other metal constituents occurred prompted a similar series of leach tests using sodium sulfide as a metallic sulfide precipitant. Arsenic extraction in caustic leaches containing large excesses of sodium sulfide was found to be nearly complete (Table 22).

TABLE 22. ARSENIC EXTRACTION BY SODIUM HYDROXIDE IN THE PRESENCE OF SULFIDE ION

Sodium hydroxide Molarity	Sodium sulfide, kg/kg dust	Arsenic extraction, %
1	0.24	94.8
2	0.24	100.0
2	0.24	97.2
2	0.24	99.2
2	0.15	96.9
3	0.24	99.1

The arsenic extraction data given in Table 22 were based on residue assays only. However, allowing for some uncertainty in analytical results, the use of sodium hydroxide in conjunction with sodium sulfide would appear to constitute a very effective lixiviant for arsenical flue dusts of low sulfide content. In the event that arsenic-bearing sulfide mineral remnants were present in the dusts to a significant degree, caustic leaching could be expected to be less effective, however.

Leaching with Ferric Ion Solutions--

A variety of ferric ion based lixiviants were used to determine the leaching characteristics of flue dust sample SFD-C. All leach tests were performed at 10 percent solids pulp density.

Ferric Chloride Leach Results--

The results of leach tests using 0.5 molar ferric chloride showed moderate to good extraction of arsenic (Table 23). At elevated temperatures, arsenic solubility increases substantially over that obtained at room temperature although the data given in the table indicate that the leach solution became saturated with

TABLE 23. FERRIC CHLORIDE* LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Temp, ^oC	Sample Time, Hr	Sample Product	Analysis, % or gpl					Distribution, %				
			As	Cu	Zn	Cd	Bi	As	Cu	Zn	Cd	Bi
25	0.5	Solution	13.1	2.72	12.8	0.64	0.24	38.5	62.1	90.2	84.7	43.4
		Residue	38.0	3.01	2.54	0.20	0.57	61.5	37.9	9.8	15.3	56.6
25	3.0	Solution	13.8	2.76	12.6	0.60	0.28	41.2	64.4	90.4	85.0	52.1
		Residue	37.7	2.91	2.56	0.20	0.49	58.8	35.6	9.6	15.0	47.9
85	0.5	Solution	32.1	3.86	13.5	0.76	1.05	86.3	79.2	91.8	88.8	84.5
		Residue	15.0	2.96	3.54	0.29	0.56	13.7	20.8	8.2	11.2	15.5
85	3.0	Solution	53.0	14.1	52.1	2.56	1.58	44.3	88.7	94.2	91.5	87.4
		Residue	39.0	1.05	1.89	0.14	0.13	55.7	11.3	5.8	8.5	12.6

* 0.5 Molar $FeCl_3$

respect to arsenic through evaporation loss of water from the leach vessel. Together with arsenic, however, rapid and nearly complete dissolution of other constituents of the flue dust took place as well. The weight loss observed during leaching indicates that ferric chloride acts as a solvent for the flue dust as a whole.

Acid Ferric Chloride Leach Results--

The addition of hydrochloric acid to solutions used for flue dust leaching does not significantly alter the leach results obtained without deliberate acid addition (Table 24). As before, the flue dust tends to dissolve in bulk rather than showing any particularly selective response. Increased temperature promotes leaching to such an extent that the dust sample is nearly totally consumed within three hours.

Ferric Sulfate Leach Results--

The use of ferric sulfate in place of ferric chloride as a leaching agent produces almost identical results (Table 25). Leach extraction of all components of the dust was found to be moderate to good with the highest degree of solubilization occurring at the higher temperature and longer times. The single exception was that bismuth solubility did not appear to increase at elevated temperatures but, rather, showed a slight decrease of the results obtained at room temperatures.

Acidic Ferric Sulfate Leach Results--

The addition of sulfuric acid to solutions of ferric sulfate shows virtually no effect on the leach results obtained using ferric sulfate alone (Table 26).

TABLE 24. ACIDIC FERRIC CHLORIDE* LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Temp, °C	Sample Time, Hr	Sample Product	Analysis, % or gpl					Distribution, %				
			As	Cu	Zn	Cd	Bi	As	Cu	Zn	Cd	Bi
25	0.5	Solution	11.8	2.80	11.8	0.24	0.90	35.8	63.8	90.7	57.5	87.9
		Residue	41.8	3.14	2.41	0.35	0.24	64.2	36.2	9.3	42.5	12.1
25	3.0	Solution	13.6	2.76	12.4	0.22	0.94	44.2	66.8	91.2	59.5	91.0
		Residue	39.0	3.11	2.46	0.34	0.21	55.8	33.2	8.8	40.5	9.0
85	0.5	Solution	35.4	4.12	14.4	0.78	1.18	96.5	83.7	96.9	97.4	98.3
		Residue	10.5	6.5	3.69	0.21	0.21	3.5	16.3	3.1	2.6	1.7
85	3.0	Solution	58.8	7.08	28.5	1.56	2.40	72.9	90.7	98.0	96.2	97.2
		Residue	36.8	1.23	0.96	0.10	0.11	27.1	9.3	2.0	3.8	2.8

* 0.5 Molar $FeCl_3$ + 0.5 Molar HCl

TABLE 25. FERRIC SULFATE* LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Temp, °C	Sample Time, Hr	Sample Product	Analysis, % or gpl					Distribution, %				
			As	Cu	Zn	Cd	Bi	As	Cu	Zn	Cd	Bi
25	0.5	Solution	12.4	2.68	13.4	0.65	0.78	38.0	64.9	90.5	85.1	46.8
		Residue	34.3	2.60	2.35	0.19	1.48	62.0	35.1	9.5	14.9	53.2
25	3.0	Solution	12.4	2.74	13.4	0.64	0.82	40.7	63.1	91.5	86.8	51.5
		Residue	32.0	2.84	2.22	0.17	1.37	59.3	36.9	8.5	13.2	48.5
85	0.5	Solution	33.3	3.70	14.6	0.72	0.41	92.9	74.7	91.2	86.1	32.2
		Residue	6.8	3.36	3.78	0.30	2.34	7.1	25.3	8.8	13.9	67.8
85	3.0	Solution	27.2	5.34	21.0	1.12	0.61	57.3	79.0	89.1	88.7	36.7
		Residue	21.8	1.51	2.47	0.15	1.11	42.7	21.0	10.9	11.3	63.3

* 0.5 Molar $Fe_2(SO_4)_3$

TABLE 26. ACIDIC FERRIC SULFATE* LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Temp, °C	Sample Time, Hr	Sample Product	Analysis, % or gpl					Distribution, %				
			As	Cu	Zn	Cd	Bi	As	Cu	Zn	Cd	Bi
25	0.5	Solution	12.6	2.90	14.2	0.67	0.50	36.6	67.2	91.9	90.3	42.2
		Residue	38.0	2.46	2.18	0.13	1.20	63.4	32.8	8.1	9.7	57.8
25	3.0	Solution	11.6	2.68	12.8	0.66	0.49	35.9	61.2	91.5	91.4	44.4
		Residue	36.0	2.96	2.07	0.11	1.07	64.1	38.8	8.5	8.6	55.6
85	0.5	Solution	31.8	3.76	13.84	0.82	0.62	85.4	73.1	91.7	93.9	45.3
		Residue	13.3	3.39	3.07	0.14	1.82	14.6	26.9	8.3	6.1	54.7
85	3.0	Solution	33.6	7.82	31.2	1.84	1.26	49.7	76.7	91.8	90.6	42.7
		Residue	26.5	1.59	1.86	0.11	0.97	50.3	23.3	8.2	9.4	57.3

* 0.5 Molar $(Fe_2(SO_4)_3$ + 0.5 Molar H_2SO_4

Ferric ion based lixiviants have been found to be effective lixiviants for the arsenic content of flue dust. The major disadvantage to their use is the fact that all of the variations examined act as quantitative solvents for the dust as a whole, producing, in effect, a liquid dust product. In view of the non-selective action of ferric salts, no further consideration was given to their use in the present study.

Leaching with Water--

The major arsenic-containing component of all the flue dust samples studied was found to be arsenic (III) oxide, which is relatively soluble in plain water. However, since most dusts contain a variety of acid forming compounds it is to be expected that simple water leaching of dusts would generate mildly acidic solutions (Table 27).

TABLE 27. NATURAL pH OF SELECTED FLUE DUST SAMPLES

Temp, °C	SFD-A	SFD-B	SFD-C	SFD-D	SFD-E
40	2.91	2.18	2.48	2.20	5.90
50	2.74	2.02	2.26	2.15	5.60
60	2.51	2.04	2.09	2.10	5.35
70	2.36	2.04	2.03	2.05	5.20

Since a considerable number of acid leach studies were to be undertaken as part of the current study, all tests performed at or near the natural solution pH of the various dusts is reserved for discussion in the following section.

Leaching with Sulfuric Acid--

Two of the flue dust samples described earlier in Table 2, SFD-B and SFD-C, were leached under varying conditions of acid strength (pH), temperature, and the results summarized (Tables 28 and 29). Both of these dusts contain large (20 to 30 percent) total concentrations of arsenic generally thought to be present in the form of arsenic (III) oxide. The data present in the tables indicate that the major portion of the arsenic is immediately soluble under all test conditions. Extending the leach time to periods of up to 1.5 hours was found to result in a variable, but relatively insignificant effect on overall extraction. Both reduced pH and increased temperature favor higher extraction but time is not considered to be an important variable. In addition to arsenic (III) oxide, both dust samples contain arsenic compounds of an indeterminant composition which are not soluble under the conditions for leaching as shown in Tables 28 and 29. X-ray diffraction analysis of the leach residues recovered from the tests showed no identifiable primary arsenic compounds.

A variety of other flue dust constituents were monitored in addition to arsenic, for the sulfuric acid leach tests presented in Tables 28 and 29. Without presenting detailed analytical results, several generalizations are worth noting. Zinc and cadmium, both presumed to be present as sulfates, were found to exhibit solubility characteristics very similar to arsenic. Following 1.5 hours of leaching, zinc and cadmium extraction typically exceeded 90 percent under all test conditions. Copper extraction, on the other hand, rarely exceeded 50 percent except for tests performed at the higher temperatures and lower pH's. Although never substantial, copper extraction was always significant and would thus pose a problem if recovery of by-products is

TABLE 28. SULFURIC ACID LEACH RESULTS FOR FLUE DUST SAMPLE SFD - B

Temp, °C	pH	Arsenic Extraction, % Time, Minutes 20	50	90
50	1.0	81.4	84.7	84.9
	1.5	76.0	80.4	79.5
	2.0	73.9	71.7	69.0
	2.5	56.9	62.4	73.0
60	1.0	90.7	90.5	86.4
	1.5	78.8	79.0	79.8
	2.0	81.3	81.2	76.2
	2.5	75.3	75.5	74.3
70	1.0	90.2	89.7	91.2
	1.5	83.5	81.9	79.7
	2.0	77.8	78.1	71.6
	2.5	73.0	74.9	72.0

TABLE 29. SULFURIC ACID LEACH RESULTS FOR FLUE DUST SAMPLE SFD - C

Temp, °C	pH	Arsenic Extraction, %		
		Time, Minutes		
		20	50	90
50	1.0	93.4	94.3	94.6
	1.5	91.8	92.7	92.0
	2.0	90.8	91.3	91.6
	2.5	89.5	90.1	89.9
60	1.0	93.6	93.6	93.4
	1.5	92.3	92.5	91.8
	2.0	91.0	91.3	89.7
	2.5	89.0	89.2	87.6
70	1.0	--	92.8	93.3
	1.5	92.0	--	91.3
	2.0	89.9	89.7	89.0
	2.5	90.0	89.0	88.0

to constitute a portion of an arsenic treatment process for such dusts. The only other dust components found to undergo partial leaching in the tests were lead and tellurium which leached to some extent at pH = 1.0.

The apparent insolubility of unidentified residual arsenic compounds present in the dilute sulfuric acid leach residues recovered from leach tests using sample SFD-C was further examined by prolonging the leach time to 165 hours. A sample of dust leached at room temperature and pH = 1.5 showed a maximum arsenic extraction of 91.5 percent which was achieved after approximately five hours of leaching. The results of similar tests conducted at higher temperatures (Table 28) were thus reproduced almost exactly.

The residue recovered from the week-long sulfuric acid leach of the flue dust sample SFD-C containing approximately 6.5 percent residual arsenic was further studied by both optical and X-ray diffraction techniques to attempt to characterize the arsenic compounds present. The mineral enargite (Cu_3AsS_4) was found in minor to trace amounts that were insufficient to account for the major portion of the arsenic indicated by chemical analysis. X-ray diffraction patterns revealed only lead sulfate but with notably distorted diffraction peaks.

An electron microprobe study of the leach residue indicated that virtually all of the contained arsenic was associated with the lead sulfate grains. Two individual lead sulfate grains were counted for their elemental constituents and the results summarized (Table 30).

TABLE 30. COMPOSITION OF SFD-C LEACH RESIDUE LEAD SULFATE GRAINS

Grain No.	Component, %					
	Pb	As	Se	Fe	S	0
1	66.66	6.95	0.10	1.77	5.80	18.78
2	60.65	6.69	0.02	1.98	10.79	19.94

The data in Table 29 indicate considerable solid substitution of arsenic in a mixture of lanarkite ($PbO \cdot PbSO_4$) and anglesite ($PbSO_4$) of variable proportions. The claim of solid substitution versus mechanical admixture is partially supported by leach tests performed using fresh makeup containing no arsenic in which no dissolution of arsenic was observed and by the distorted diffraction patterns.

Various other dust samples described in Table 2 were leached in sulfuric acid solutions at pH = 1.0 for comparison with the results obtained using samples SFD-B and SFD-C. In addition, a suite of samples was leached at an acid strength of 0.92 molar (90 grams per liter). All leach tests in this series were conducted at 70°C and 5 percent solids pulp density for four hours (Table 31).

The data given in Table 30 further indicate that all dusts examined in this study are unique in terms of leaching behavior. The three copper smelter dusts, SFD-A, SFD-D, and SFD-G, although similar in composition and conditions of generation, behave in quite dissimilar fashion when leached under identical conditions. Dusts SFD-A and SFD-G show excellent arsenic extraction when leached in hot, concentrated sulfuric acid but only dust SFD-A maintains this characteristic when the acid concentration drops

TABLE 31. SULFURIC ACID LEACH RESULTS FOR FLUE DUST SAMPLES SFD - A, - D, -E, AND - G

Dust Sample	Acid Strength	Sample Product	Analysis, % or gpl						Distribution, %					
			As	Cu	Zn	Cd	Sb	Te	As	Cu	Zn	Cd	Sb	Te
SFD-A	90 gpl	Solution	7.9	3.74	1.78	0.17	0.10	0.10	98.9	43.5	71.6	95.0	59.0	77.9
		Residue	0.4	22.4	3.29	0.04	0.32	0.13	1.1	56.5	28.4	5.0	41.0	22.1
SFD-D	90 gpl	Solution	1.3	5.54	2.54	0.17	0.04	0.05	64.4	89.2	95.4	85.8	40.0	59.0
		Residue	2.3	2.14	0.39	0.09	0.19	0.10	35.6	10.8	4.6	14.2	60.0	41.0
SFD-E	90 gpl	Solution	5.1	0.11	5.90	0.52	0.42	0.003	89.6	93.0	96.0	91.1	19.7	--
		Residue	1.4	0.02	0.59	0.12	4.05	<0.01	10.4	7.0	4.0	8.9	80.3	--
SFD-G	90 gpl	Solution	9.3	3.18	0.72	0.06	0.04	0.02	98.8	92.6	84.5	100	35.9	--
		Residue	0.11	0.26	0.13	ND	0.08	ND	1.2	7.4	15.5	--	64.1	--
SFD-A	pH 1.0	Solution	8.1	1.94	1.68	0.17	0.01	0.04	95.8	22.8	67.0	91.2	6.6	32.0
		Residue	1.3	23.8	3.00	0.06	0.50	0.31	4.2	77.2	33.0	8.8	93.4	68.0
SFD-D	pH 1.0	Solution	1.5	3.48	2.42	0.17	0.01	0.01	75.2	54.2	88.1	84.2	3.0	12.6
		Residue	1.4	8.3	0.93	0.09	0.47	0.16	24.8	45.8	11.9	15.8	97.0	87.4
SFD-E	pH 1.0	Solution	4.6	0.09	5.42	0.46	0.09	ND	85.0	79.4	94.0	88.8	4.8	--
		Residue	2.1	0.06	0.90	0.15	4.60	ND	15.0	20.6	6.0	11.2	95.2	--
SFD-G	pH 1.0	Solution	1.4	2.72	0.57	0.04	0.01	0.01	78.7	78.2	66.3	78.2	--	--
		Residue	0.9	0.76	0.29	0.01	ND	ND	21.3	21.8	33.7	21.8	--	--

to that equivalent to pH = 1.0. Dust SFD-D, on the other hand, actually leaches more completely in dilute acid than in concentrated acid. The lead smelter dust, SFD-E shows moderate arsenic solubility which is nearly insensitive to acid concentration between the limits examined.

The data in Table 31 also show that the leaching characteristics of other components of the dusts are equally as erratic as that of arsenic. Elements such as lead, bismuth, and tin are not described in Table 31 due to solubilities which were found to be either uniformly low or near zero.

Attempts to standardize the leaching responses of many different dusts were quickly resolved to the single choice of sulfatization via concentrated sulfuric acid. By heating metallic sulfides or oxides with specific quantities of sulfuric acid under appropriate conditions, essentially water soluble sulfates can be formed that results in a normalization of leaching characteristics.

$$M_xO_y + yH_2SO_4 \rightarrow M_x(SO_4) + yH_2O$$

$$M_xS_y + 2yH_2SO_4 \rightarrow M_x(SO_4)_y + yS + ySO_4 + 2yH_2O$$

Since most smelter flue dusts are of indeterminant mineralogical composition however, the required amount of acid, temperature, and digesting time must be determined by trial-and-error although, generally speaking, an inverse relationship exists between reaction temperature and time. Reaction temperatures in excess of 250°C are seldom found to be effective due to vaporization of sulfuric acid. Sulfatizing at temperatures in excess of

200°C results in significant vaporization losses of arsenic (III) oxide which rapidly increase with temperature. Being water soluble, such arsenical fumes can be easily recovered by scrubbing with make-up leach liquor and, thus, present no particular problem in treatment utilizing sulfatization-leaching techniques.

As an example of the effect prior sulfatization has on subsequent leaching behavior, flue dust samples SFD-A, -D, -E, and -G were leached with concentrated sulfuric acid in a ratio of one part dust to 0.8 part acid and the mixtures heated at 200°C for 1.5 hours. After cooling to room temperature, the products were leached in water for four hours at 65° to 70°C and the results summarized (Table 32).

TABLE 32. LEACH RESULTS FOR FLUE DUST SAMPLES AFTER SULFATIZATION

Dust	Extraction, %									
	As	Cu	Zn	Cd	Fe	Pb	Sn	Sb	Bi	Te
SFD-A	96.5	98.2	97.3	96.9	95.4	0.9	0.0	18.6	11.2	30.4
SFD-D	91.5	99.1	98.8	93.7	85.5	0.2	0.0	10.7	10.5	16.2
SFD-E	70.8	96.6	99.2	91.6	20.6	0.0	0.0	3.1		
SFD-G	82.6	92.8	84.5	96.3	36.9	2.1	0.0	18.3	13.8	44.4

The results shown above indicate that sulfatization prior to leaching can have a marked effect on the solubility characteristics of smelter flue dusts. Dust sample SFD-A does not respond to sulfatization in regard to arsenic extraction (see Table 31), but does yield considerably better results with respect to copper and zinc extraction when pretreated with sulfuric acid. Sample SFD-D shows a marked improvement in the leach extraction of arsenic as well as copper and zinc compared with the results obtained by sulfuric acid alone, particularly when compared with the results obtained at moderate pH. Dusts SFD-E and SFD-G did not respond to sulfatization in regard to arsenic extraction although the leach results given in Table 32 are comparable to those shown in Table 31 at moderate pH.

The data given in Tables 31 and 32 indicate that most smelter flue dusts respond well to a combination of sulfatization followed by either water or sulfuric acid leaching. The added advantage of nearly complete extraction of copper, zinc, and cadmium favors the use of sulfuric acid as opposed to the other reagents examined by providing a degree of segregation of other dust constituents in addition to nearly complete arsenic extraction. In this way, a sizable fraction of the original dust containing a variety of impurities deleterious to most nonferrous smelting operations can be isolated from the arsenic as well as several important metals of value. Such a solid residue constitutes an important means of impurity rejection in most smelting operations.

Arsenic Removal Studies

The various leaching studies described in the previous section were found to be moderately to nearly completely successful in extracting the arsenic content of the several different types of smelter flue dusts examined in the present study. The use of sulfuric acid as a lixiviant appears to offer the most expeditious solution to the combined problems of arsenic extraction and leach selectivity. Having produced an aqueous solution containing the bulk of the arsenic content of a smelter flue dust, however, it becomes necessary to devise a procedure for recovering arsenic from solution in such a form as would constitute an environmentally safe compound for disposal. The concomittant recovery of other constituents of the leach solutions, whether necessary or desirable, is beyond the scope of the present investigation, however, and will not be considered further. The detailed leach results presented in the preceding discussion are offered only as a guide for the leach behavior of other constituents.

A comprehensive survey of arsenic-related literature reported in the current study by Mehta, 1981 (6) indicates that arsenic may be recovered quantitatively from solutions of either arsenious or arsenic acid by coprecipitation with ferric compounds. If fully oxidized to As (V), stoichiometric ferric arsenate may be precipitated by suitable adjustment of solution pH. Present as As (III) oxide, arsenic can be precipitated with ferric hydroxide by means of chemisorption. Either method can yield residual arsenic concentrations on the order of one part per million or less.

Arsenic Removal by Coprecipitation with Iron Compounds--

The various tests performed to examine the removal of arsenic from leach solutions were conducted using a pregnant filtrate obtained from strong sulfuric acid leaches made using smelter flue dust Sample SFD-A. Several leach filtrates were prepared of approximately equal composition, partially neutralized to pH 2 with calcium carbonate, and substantially decopperized prior to arsenic precipitation.

Neutralization of excess free sulfuric acid with calcium carbonate was found to be an effective means of purifying the leach solutions of minor dissolved impurities such as bismuth, antimony, and tellurium which invariably leach to some extent in strongly acidic solution. Whether removed by direct precipitation or chemisorption, residual levels of these impurities were consistently found to be below one part per million at pH 2. Decopperizing of the leach solutions in preparation for arsenic removal was effected by solvent extraction so as not to alter the composition of the solutions through the addition of potentially reactive solutes. The specific techniques used to accomplish decopperization are beyond the scope of the present study and are not considered further. The approximate compositions of solutions used for arsenic precipitation are summarized in Table 33.

TABLE 33. COMPOSITION OF FEED SOLUTIONS USED FOR ARSENIC PRECIPITATION

Component	Concentration, gpl
As	4 - 5
Cu	0.3 - 1.0
Fe	10 - 12
Zn	2.5 - 3.0
Cd	0.2 - 0.3
Pb, Sn, Sb, Bi, Te	<0.001

Arsenic was removed from solution by increasing the pH with calcium carbonate additions to yield a final solution barren of iron (<0.001%) at pH 5. Arsenic levels of 15 to 20 parts per million were reproducibly obtained under all conditions of temperature and time if the hydrolysis of ferric sulfate was carried to completion. At room temperature, 4 to 5 hours was sufficient to complete the reaction. Final stripping of arsenic to as low as 0.05 parts per million was achieved by prolonged agitation with small amounts of calcium phosphate but the results showed no reproducibility.

X-ray diffraction studies on the precipitates produced by the procedure outlined above failed to indicate any specific arsenic-bearing compounds. All patterns obtained indicated major amounts of gypsum with indistinct "halos" characteristic of cryptocrystalline or amorphous phases. Ferric arsenate, if indeed present, could not be verified by diffraction studies.

In order to gain some insight into the characteristics of the arsenical precipitates produced in the tests described above, a series of percolation leaching tests were begun to determine the long range solubility of such material. Three separate columns were assembled as depicted in Figure 6. The arsenic-bearing precipitates used for the percolation tests were produced according to the procedure outlined above with minor differences. Material for Column No. 1 was generated by slow (6 hours) hydrolysis of ferric sulfate-arsenious acid solution using calcium carbonate at 40° to 50°C to pH 6.5. The resultant precipitate was thoroughly washed in distilled water, reslurried, and loaded into the column after minor pH adjustment with sodium hydroxide. During the life of the column, the pH of the continuously recirculated leach solution decreased to 6.5 ±0.2. Samples of the leachate were infrequently withdrawn and analyzed for arsenic content (Figure 7). Except for an initial decay from about 15 to 20 parts per million arsenic, the leach solution maintained a relatively consistent level of 7 to 8 parts per million arsenic. Flushing of the column with pure water after 71 days was followed

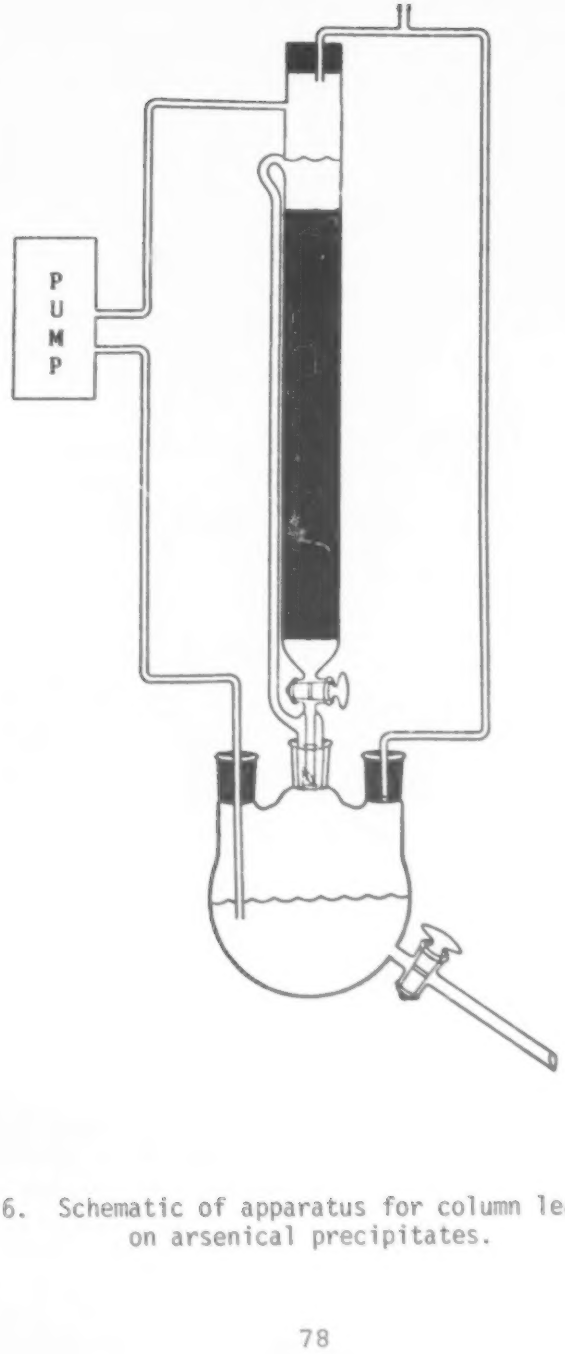


Figure 6. Schematic of apparatus for column leaching tests on arsenical precipitates.

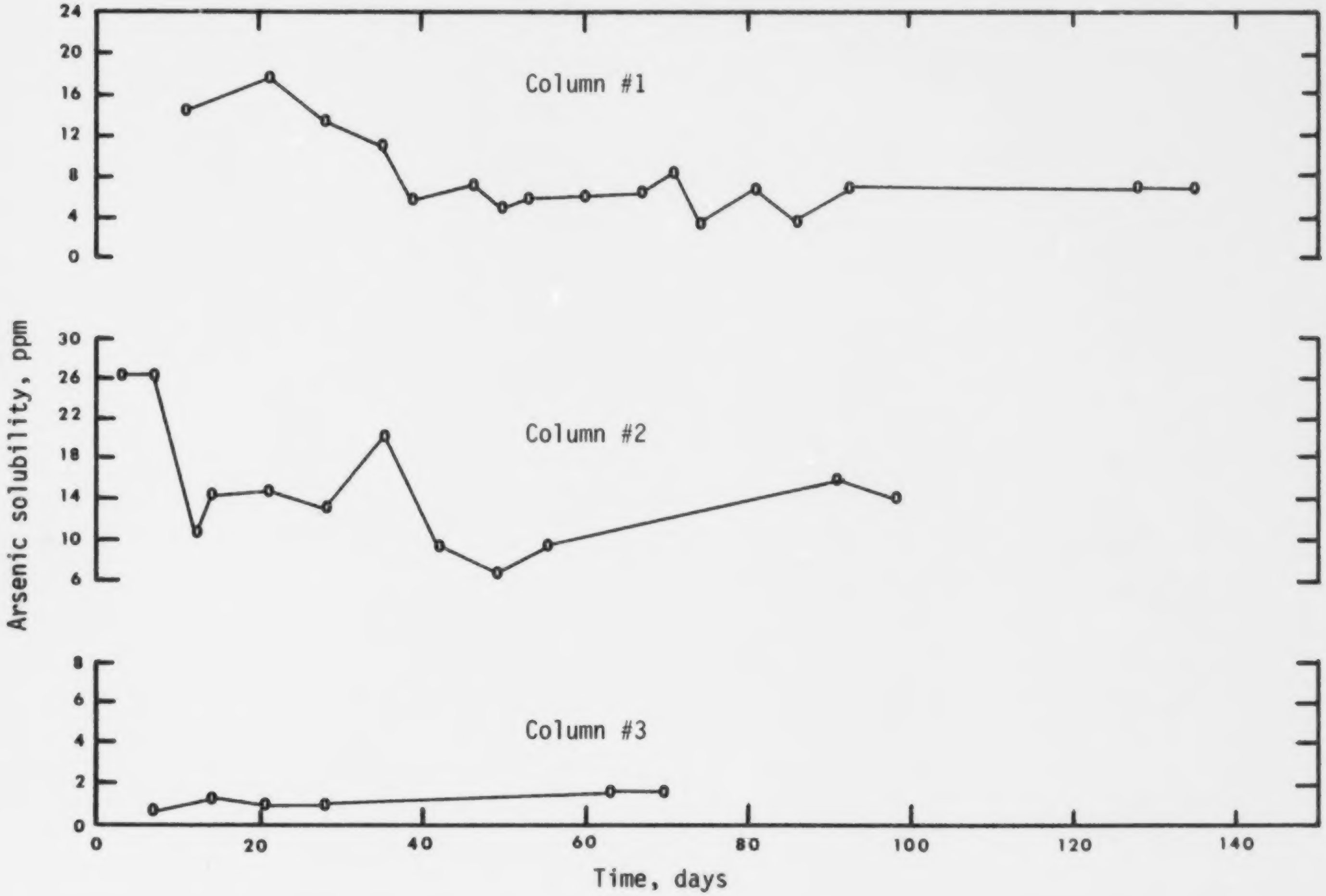


Figure 7. Solubility characteristics of arsenical precipitates.

by a reestablishment of approximately 7 parts per million arsenic within about one week.

A second column was prepared similarly to the first with the exception that 50 percent by weight of a natural calcium phosphate (collophanite) was added to the arsenic precipitate prior to increasing the slurry pH to 11.5.

AMBIENT TEMPERATURE FIXATION

Flue Dust Leach Tests

Three samples of flue dust (approximately 3.4 g each) were mixed with one liter of 1N H_2SO_4, 1N NaOH, and demineralized H_2O in polyethylene vessels and continuously stirred with a magnetic stirrer. At various time intervals, the Eh and pH were measured during the stirring. The stirring was discontinued and, after allowing the suspended solids to settle, 50 ml aliquots were transferred to plastic vessels. These samples were centrifuged and 25 ml pipetted into 100 ml pyrex volumetrics. The pH of the liquids was adjusted to approximately three by aqueous NaOH or HCl and the volume adjusted to 100 ml with demineralized water.

Upon adjustment of the pH to three, a light-green (with blue tint) precipitate formed in the second through the fifth and last NaOH leach solutions and the fifth H_2SO_4 leach solution. A red-brown precipitate formed in the fourth H_2SO_4 leach solution; probably the result of adjusting the pH to too high a value, thereby causing the precipitation of hydrated iron III oxide.

The concentration of arsenic, pH and Eh data for these leach solutions are noted in Table 34.

TABLE 34. ARSENIC FLUE DUST LEACHATE pH AND Eh DATA

Leach solution	No.	Time	Eh (mv)	pH	ppm arsenic
H_2SO_4	1	3 h, 30 min	317	1	250
	2	14 h, 45 min	322	0.6	265
	3	17 h, 0 min	332	0.6	270
	4	41 h, 15 min	363	0.6	190
	5	8 days, 5 h, 5 min	-	0.6	260
H_2O	1	3 h, 30 min	267	3.3	125
	2	14 h, 45 min	255	2.4	145
	3	17 h, 0 min	275	3.0	150
	4	41 h, 15 min	275	3.28	190
	5	8 days, 5 h, 5 min	-	3.0	195
NaOH	1	3 h, 30 min	-283	13.2	240
	2	14 h, 45 min	-228	13.4	240
	3	17 h, 0 min	-220	12.95	230
	4	41 h, 15 min	-85	13.3	215
	5	8 days, 5 h, 5 min	-	13.2	205

In an attempt to determine whether the presence of the precipitate (formed upon pH adjustment of the leach liquids) had an effect upon lowering the experimentally observed concentration of As in the liquid phase, HCl, or $NaOH_{(aq.)}$ were added to the leach liquids which contained a precipitate. HCl was added to the fourth and fifth H_2SO_4 leach solutions and $NaOH_{(aq.)}$ to the second through fifth NaOH leach solutions. The concentration of arsenic (corrected for the volume changes) is presented in Table 35.

TABLE 35. CORRECTED AS FLUE DUST LEACHATE CONCENTRATIONS

Leach solution	No.	PPM As		Effect upon precipitate
		Before	After	
H_2SO_4	4	190	262	Red-brown ppt dissolved
	5	260	261	Light-green ppt dissolved
NaOH	2	240	233	Light-green ppt partially dissolved
	3	230	243	Light-green ppt partially dissolved
	5	205	261	Light-green ppt partially dissolved

These new concentration data were used to replace those obtained in the leach solutions prior to addition of the acid or base. Using these concentrations, the amount of As extracted as a function of time was calculated and the concentration of arsenic in the flue dust was also calculated. These data are presented in Table 36.

T-36

The solid residues from these leaching systems were examined via X-ray diffraction to identify the phases present. There was no evidence of arsenolite being present in any of the three residues.

TABLE 36. AMOUNT OF ARSENIC EXTRACTED IN As FLUE DUST LEACHING TESTS

Leach liquid	No.	Cumulative mass of arsenic extracted	Calculated W/O in flue dust	Fraction of arsenic extracted
NaOH	1	0.93	-	-
	2	0.94	-	-
	3	0.97	-	-
	4	-	-	-
	5	1.04	30.87	0.97
H_2SO4	1	1.0	-	-
	2	1.06	-	-
	3	1.07	-	-
	4	1.04	-	-
	5	1.04	31.76	1.0
H_2O	1	0.48	-	-
	2	0.51	-	-
	3	0.59	-	-
	4	0.69	-	-
	5	0.74	-	0.69

It appears that the dissolution of the red-brown precipitate had a significant effect upon the concentration of arsenic. The precipitation of iron III hydroxide has reportedly been effective in removing arsenic from solution. The light-green precipitate occuring in the fifth H_2SO_4 leach liquid did not appear to have an effect upon the arsenic in solution. In contrast, the partial and complete removal of the light-green precipitate in the NaOH leach solutions by addition of $NaOH_{(aq.)}$ did, in general, appear to result in an increase in the arsenic concentration. The slight decrease in the No. 2 NaOH leach solution is not understood. It is possible that this phenomenon and that observed in the No. 5 H_2SO_4 leach solution could be explained by the adsorption of arsenic on the surface of the precipitate and the competition for available adsorption sites by either the SO_4^{-2} or other components of varying concentrations in the leach solutions.

The amount of arsenic extracted as a function of time indicates that the extraction is essentially complete after about 17 hours in the H_2SO_4 and the NaOH leach systems. In contrast, the extraction with water is not complete even after eight days, as evidenced by the 69 percent of the total extracted by the H_2SO_4 solution.

Arsenic Fixation Tests

The initial fixation studies with the arsenic flue dust leachate solutions were difficult to interpret. It would appear that the As sorption capability of each solid is quite sensitive with respect to the total chemistry of the solutions. It is noted that the ratio, i.e., mass of arsenic initially in solution to the mass of the solid, is essentially constant for all three leachate solutions, namely, 0.10, 0.12, and 0.11 for the H_2O, NaOH, and H_2SO_4 leach solutions, respectively. The variation in sorption properties of any one solid in these solutions may be primarily due to the initial pH of the solution, which is recorded in Table 34 as 0.6, 3.0, and 13.2 for the H_2SO_4, H_2O, and NaOH leach solutions, respectively. If the Eh v.s. time is plotted, it would appear that the H_2SO_4, H_2O, and NaOH leach solutions had attained an Eh which indicates the presence of the H_3AsO_4, $H_2AsO_4^-$, and AsO_4^{-3} as the predominate ions, respectively (Figure 8). It should be noted that a qualitative test for the As (V) species was not performed and there is no direct evidence that the oxidation kinetics are sufficient to completely oxidize the As (III) ion from the flue dust within the required time of eight days. But it appears safe to assume that the H_2SO_4 leach solution contains the H_2AsO_4, and H_3AsO_3, as the predominate forms of arsenic. The H_2O leach solution contains the $H_2AsO_4^-$ and H_3AsO_3 species, and the NaOH leach solution contains the AsO_4^{-3} and $HAsO_3^{-2}$ species.

The comparison of the data in Table 34 with the pH and predominate arsenic species in the leach solutions indicates an increasing As fixation of the Cottrell dust with decreasing pH.

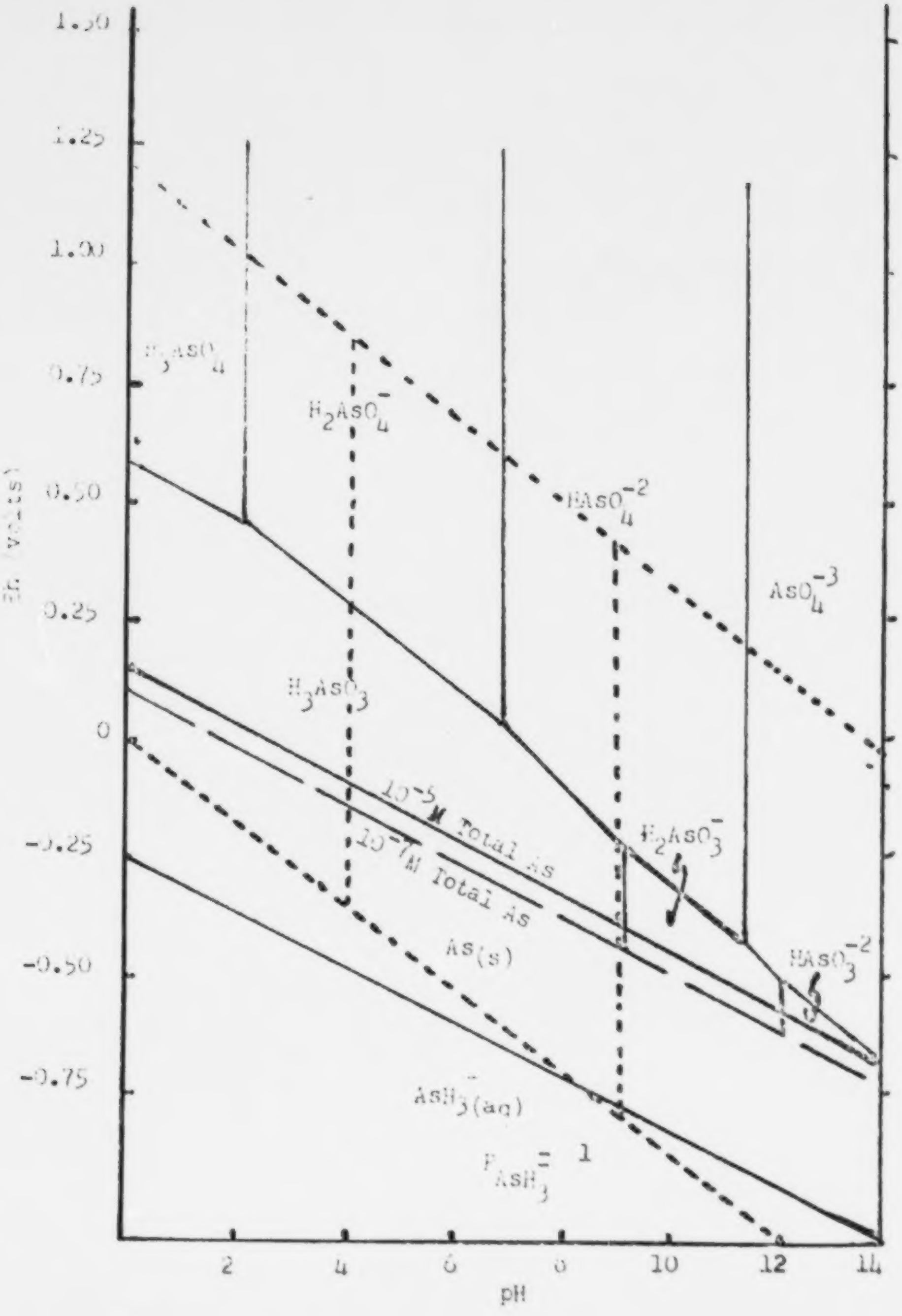


Figure 8. Eh-pH diagram for soluble arsenic species.

Since the calcium is predominately $CaCO_3$ in the Cottrell dust, the decreasing pH of the solution liberates more Ca^{+2} ion and, thereby, causes greater precipitation of calcium arsenate and/or calcium arsenite. Thus, for the case of Cottrell dust, the ionization state of the dissolved arsenic has little effect. The data for bentonite fixation indicate a contribution of arsenic from the solid phase itself. Bentonite has a concentration of 0.25 percent As and that both the H^+ ion and the OH^- ion are relatively efficient in electrophilic and nucleophilic attack, respectively, of the siloxane bonds, Diebold, 1973 (5). Thus, the five grams of bentonite in the H_2SO_4 and the NaOH leach solutions would be expected to contribute a significant amount of arsenic to the aqueous phase, e.g., a maximum increase of 250 ppm. Here, bentonite is acting as an anion absorber in the H_2O leach solution, Mehta, 1981 (6), and therefore, its sorptive capacity is sensitive to the concentration of the As (V) species and its state of ionization. A similar mechanism has been suggested for the role of phosphate rock (3), i.e., adsorption of As (III) on the surface of apatite and absorption (replacement of PO_4^{-3} radical) by As (V). Adsorption of As (III) by phosphorite increases with increasing pH due to the increase of AsO_3^{-3} ions and that a solid solution forms with AsO_4^{-3}. Data in Table 37 indicate a higher sorption in the H_2O leach solution, compared to that in the NaOH leach solution, but the fixation test with the most acidic media, i.e., the H_2SO_4 leach solution, illustrates not an increased loss of arsenic but actually a contribution of

TABLE 37. As FIXATION TESTS: As FLUE DUST - AQUEOUS SOLUTION
(2 h mix, dry, 2 h leach)

	1 N H_2SO_4		1 N NaOH	
Solid	R	Δ%	R	Δ%
Bentonite	0.0063	-21.0	0.0068	11.2
	0.0033	-38.8	0.0034	0.4
	0.0016	-45.6	0.0017	-25.3
	0.0011	-52.8	0.0012	-34.0
Cottrell	0.0065	7.8	0.0058	-13.9
	0.0032	22.8	0.0038	-29.7
	0.0016	-3.8	0.0017	-11.1
	0.0012	-99.3	0.0011	-8.9
Phosphate	0.0069	17.9	0.0069	3.0
	0.0033	22.9	0.0037	10.6
	0.0016	19.7	0.0017	0.6
	0.0012	23.0	0.0013	6.0

$$R = \frac{\text{mass of arsenic in solution}}{\text{mass of solid sorbent}}$$

Δ% = percent decrease of arsenic solution concentration due to fixation.

arsenic, i.e., the percent change of +24.6 percent. The arsenic concentration of 0.74 percent in the phosphate rock can result in a maximum increase of 740 ppm As in the aqueous phase. The increased solubility of calcium phosphate in an acidic media would explain this difference in percent change of arsenic experienced in the H_2O leach and that in the H_2SO_4 leach solutions.

An attempt was made to perform leaching tests with the residue obtained by filtering the fixation media. The residue was not washed after filtering but was added to a flask, 50 ml of water added and mixed for six hours. The data resulting from these leaching studies of the residue from the fixation tests with the As flue dust H_2O leachate are presented below.

As fixed phosphate rock	30 ppm As
As fixed bentonite	48 ppm As
As fixed Cottrell dust	4 ppm As

This represents a relatively small concentration of arsenic compared to that initially in the As flue dust H_2O leachate. But any interpretation of these data would be open to considerable doubt. There is no way to know what contribution of As emanates from the leachate solution left with the residue. In addition, it is extremely difficult to make a quantitative transfer of residue from the filtering apparatus to the leaching flask.

Due to the uncertainty in interpreting the flue dust leachate fixation data with respect to extreme range of pH and to the complex matrix generated by partial absolution of the As flue dust, the second series of fixation tests were conducted with standard As (III) and As (V) solutions. The data in Figure 9 are those generated by mixing for 24 hours the three solids with the standard As (III) solutions of varying concentration. The data in Figure 10 are generated by mixing the solids with the various As (III) solutions for two hours followed by a drying step and a residue leach for two hours. The argument for employing the drying step followed by the leach of the residue is based upon the difficulty of obtaining interpretable leach data from the filtrate of a fixation test. Thus, the leaching of the dryed residue emanating from a fixation test simulates the leaching of the arsenic fixed solid.

Figure 9 illustrates an unusual phenomenon in that the Cottrell dust becomes less capable of fixing arsenic (III) with decreasing initial concentration of arsenic. Cottrell dust also illustrates a similar trend after an initial increase in arsenic (V) solutions. This decrease is probably due to the increased acidity of the higher arsenic concentration solutions and, thus, the greater solubility of the calcite in the Cottrell dust. This same interpretation was made for the Cottrell fixation of arsenic in the As flue dust leachates. The data in Figure 10 generated from the leaching of the As fixed Cottrell dust are not fully understood. The As concentration in the leachates for the As (III) solutions actually shows a decrease with decreasing initial As concentrations in the standard solution, whereas, that for Cottrell dust in As (V) solutions shows just the opposite trend.

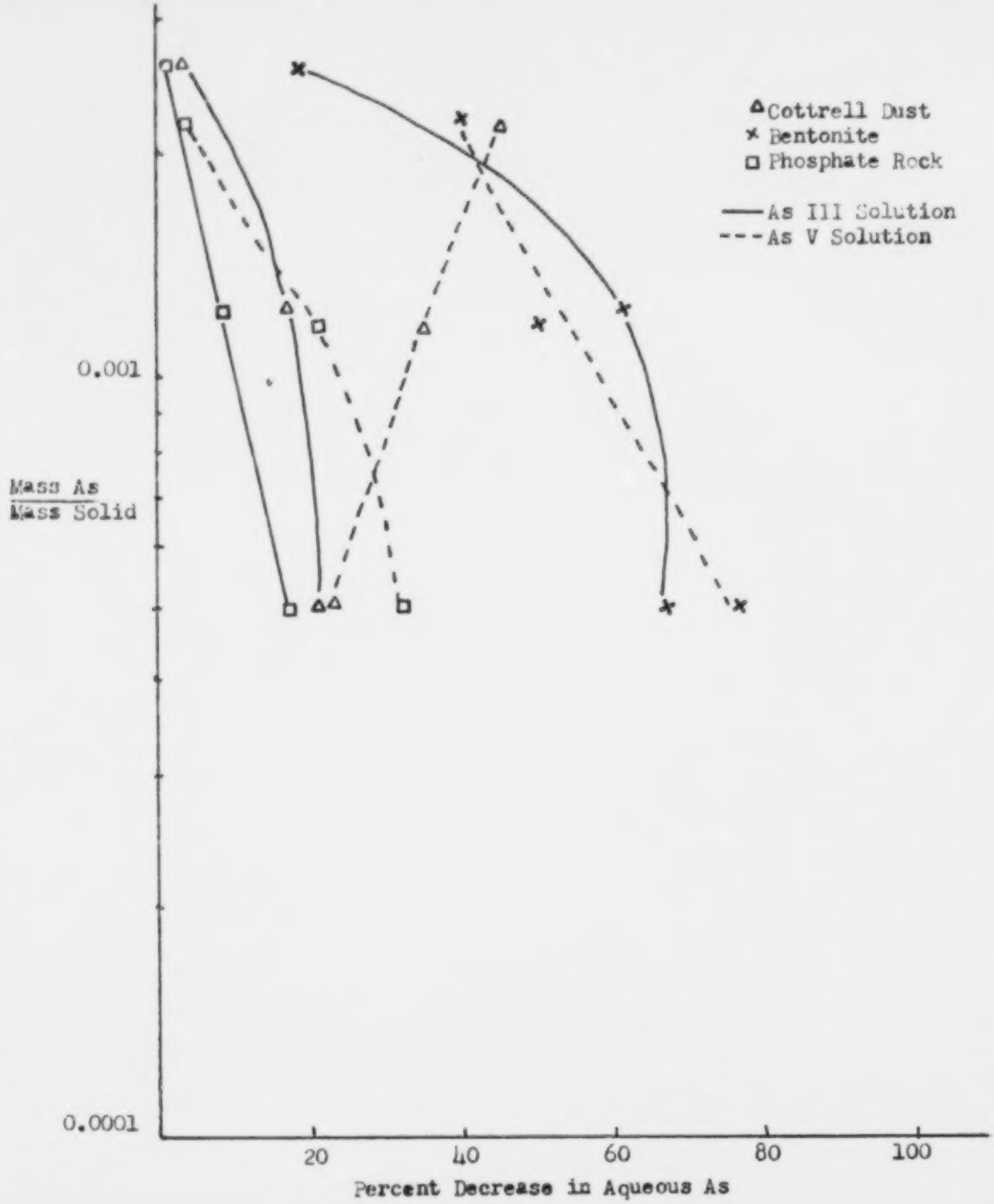


Figure 9. Standard As (III) and (V) solution fixation tests (24 hour mix).

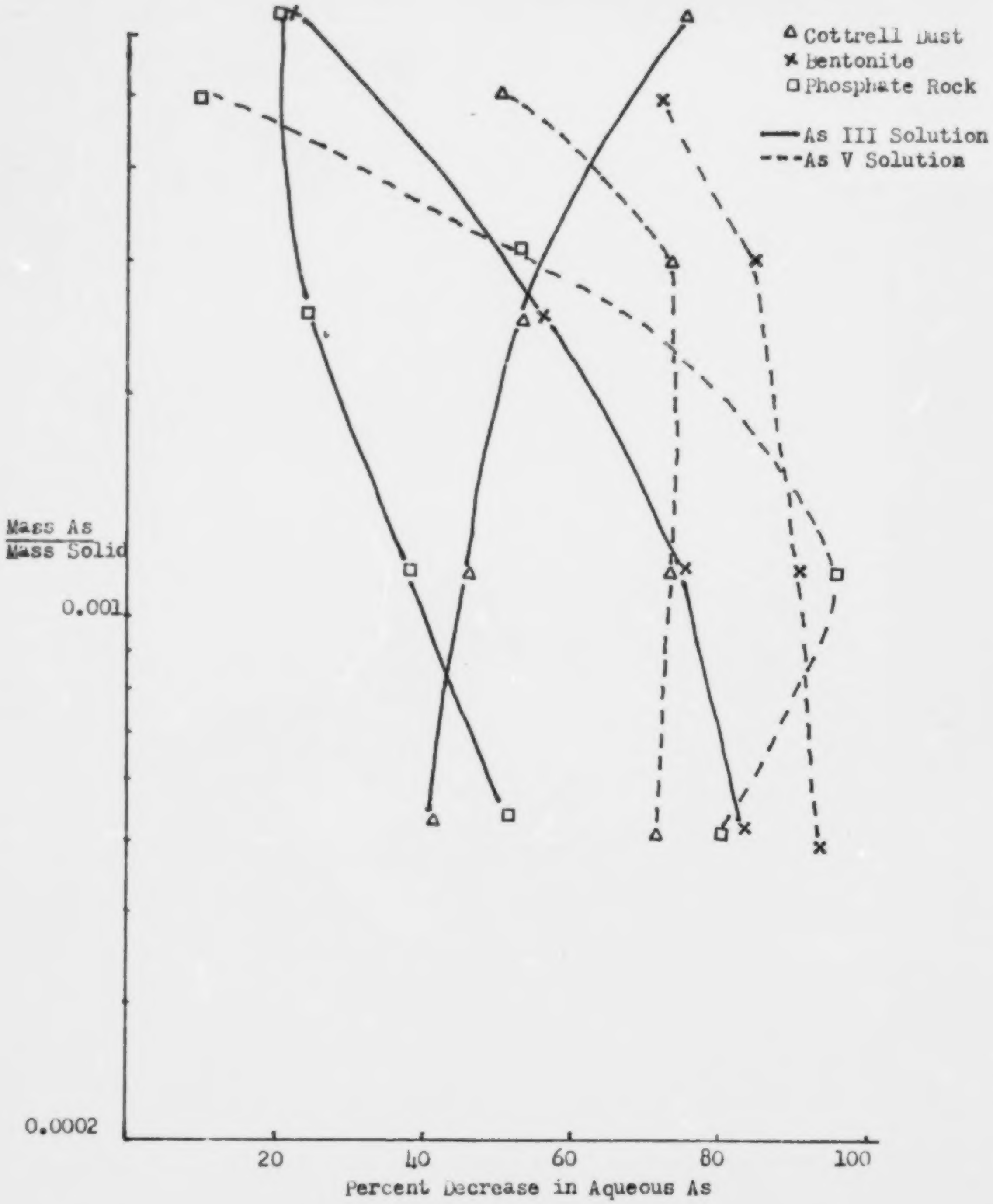


Figure 10. Standard As (III) and (V) solution fixation tests (2 hour mix - dry - 2 hour leach).

The explanation may be that since Cottrell dust is capable of fixing less As (III) with decreasing As concentration, this larger amount of As (III) remaining non-fixed, i.e., not as calcium arsenate or arsenite, is volatilized during the drying step. Therefore, one would expect to see less arsenic liberated in the aqueous phase used to leach the dried residue. The opposite effect is seen in the As (V) systems due to the difference in the volatility of non-fixed As (V) compared to non-fixed As (III).

It certainly is evident that phosphate rock and bentonite are more efficient sorbers of As (V) than of As (III) and are more capable of encapsulating As (V) than As (III) as evidenced by the concentrations of arsenic in the leachate of the As fixed phosphate residue. Bentonite does appear to have the greatest arsenic sorption capacity but the encapsulating capability of bentonite appears to be rivaled by phosphate rock, especially the As (V) fixed phosphate. The extrapolation of these data in Figure 10 would indicate that, in order for the sorption and encapsulation of arsenic to result in a 0.05 ppm As in the leachate solutions, the ratio of mass of arsenic to mass of bentonite must be approximately 0.00001 for a solution initially containing 250 ppm As (V) and 0.00001 for a solution initially containing 250 ppm As (III).

The results of the third series of fixation tests with aqueous suspension of As flue dust in the acidic and basic media are somewhat disappointing. As noted in Tables 37 and 38 , there

TABLE 38. ARSENIC FIXATION TESTS: ARSENIC FLUE DUST - AQUEOUS SOLUTION (24 hour mix)

	1 N H_2SO_4		1 N NaOH	
Solid	R	Δ %	R	Δ %
Bentonite	0.0080	-28.9	0.0065	1.0
	0.0037	- 9.7	0.0032	6.0
	0.0019	-20.6	0.0016	-1.8
	0.0012	-22.9	0.0011	2.3
Cottrell	0.0078	3.7	0.0066	-3.8
	0.0037	0.3	0.0032	-1.7
	0.0019	-84.3	0.0016	-1.0
	0.0013	-96.6	0.0012	-16.6
Phosphate	0.0076	-5.7	0.0068	-23.0
	0.0037	-3.2	0.0032	0.9
	0.0019	3.2	0.0016	-8.2
	0.0013	-2.2	0.0013	-21.7

appears to be a significant amount of variability in the data. This is probably due to the difficulty of obtaining such small samples (1 g to 6 g) that are representative of the arsenic flue dust.

Bentonite does exhibit a definite trend of increasing sorption capacity with increasing amount of bentonite. It should be noted that, in both the H_2SO_4 and NaOH solutions, the reduction of arsenic is larger in the case of encapsulation of arsenic, i.e., the two hour mix followed by drying the mixture and a two-hour leach.

The largest decrease in aqueous arsenic is for the fixation by Cottrell dust in the acid media. This, as noted earlier, is expected on the basis of the mechanism of acid dissolution of the calcite and the subsequent precipitation of calcium arsenate and/or calcium arsenite.

ELEVATED TEMPERATURE FIXATION

Slags

Solvent Considerations--

The solvents chosen for study are based on two primary considerations:

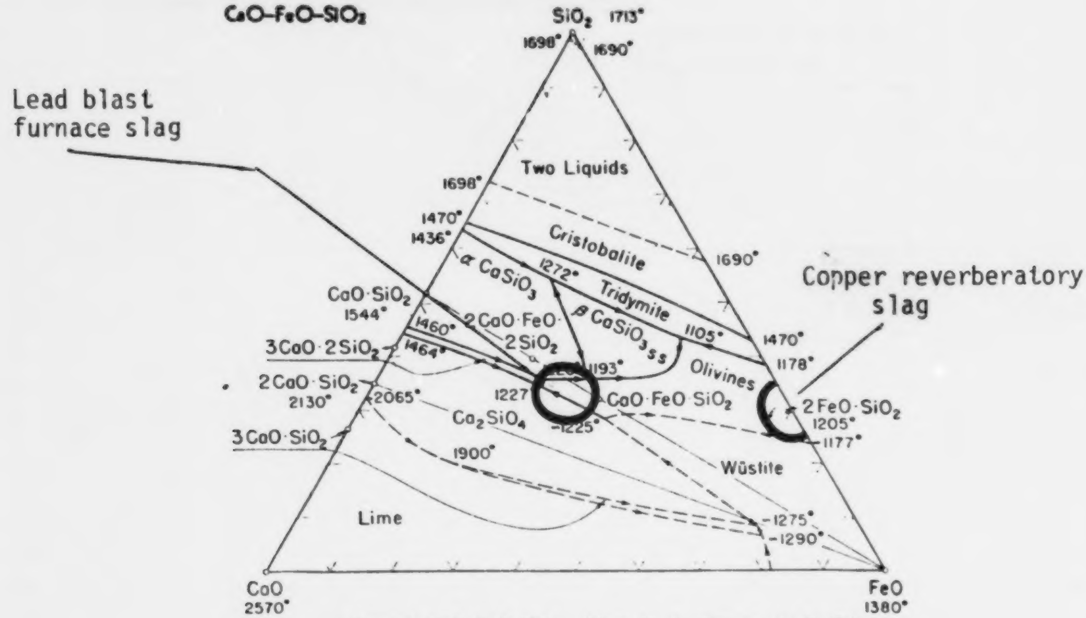
1. The availability and low cost of the materials
2. The potential for high arsenic dissolution

The first of these considerations is fulfilled by both by-product slags from smelting operations and impure clays. The second consideration, i.e., the concentration of arsenic that can be dissolved, can only be postulated because only a few phase diagrams are available for arsenic containing systems.

These considerations are no more important than the requirement for the solvents to retain arsenic in such a way as to restrict its release to the environment. This requirement may be termed as chemical fixation of arsenic. Chemical fixation is defined for the purpose of this report as the formation of a chemically stable compound containing arsenic that upon weathering will not release arsenic to the environment in detrimental quantity. Arsenic containing glass (slag) is one of the chemical fixation possibilities.

Glasses are defined by the American Society for Testing Materials as "an inorganic product of fusion which has been cooled to a rigid condition without crystallization". For our purposes a slag will be considered a glass. Slag is a multicomponent oxide mixture generated as a by-product from many smelting operations. It is normally treated for storage either by water quenching it or slow cooling it. The water quenched product is mostly non-crystalline while the slow cooled product is a matrix of crystalline and non-crystalline phases.

Slag systems that have been given the most attention in this study are the copper reverberatory and lead blast furnace slags. Both of these slag systems are liquid at 1200° to 1250°C. Their compositions are, however, considerably different. The compositions of the major components are shown in Figure 11. The major F 11



Lead blast furnace slag

Copper reverberatory slag

—System $CaO-FeO-SiO_2$. After N. L. Bowen, J. F. Schairer, and E. Posnjak, *Am. J. Sci.*, 5th Ser., 26, 204 (1933) with the estimated relations as shown by the dashed lines added.

A. Muan and E. F. Osborn, preprint of paper presented before General Meeting of American Iron and Steel Institute, at New York, May 23–24 (1951).

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Figure 11. Slag composition.

difference in the slag compositions is the lime content, i.e., reverberatory slags contain only a few percent CaO, whereas the lead blast furnace slags contain 20 to 35 percent CaO.

Estimates of arsenic content in both slag systems at 1200° and 1400°C are presented in Table 39. These two slag systems were chosen for detailed study because they are produced at smelter sites where arsenic disposal is a problem. The slags are produced as molten products from a part of their pyrometallurgical process operations. The potential, therefore, exists to utilize an already molten product as the solvent in which to dissolve the arsenic. This would mean a tremendous savings in energy, i.e., remelting solidified slag is an expensive operation that would not be required if the slag is treated while still molten.

Solvents other than slags have also been considered (but not in as much detail), e.g., clays, power plant fly ash, phosphorus rock, phosphorus smelting slags, sodium silicate slags.

Leach Test--

The leach procedure used in all leach tests has been described in detail in previous reports, but briefly, the test consists of fixing the solid to liquid ratio at 1:100. The leach medium is distilled water equilibrated with an air environment. Its pH is about 5.7. The solid samples, usually about 8 mesh, are immersed in the distilled water and placed on a shake tester. Samples of liquid are pulled periodically and analyzed for arsenic

TABLE 39. ARSENIC CONTENT IN SLAGS

Slag	Form of Arsenate (1)	Temperature °C	Arsenic Content (%) (2)	Experimental Arsenic Concentration Achieved (%) (3)
Reverberatory (Fayalite Slag)	Ca	1200	15-25	--
	Fe	1200	10-15	--
	Ca	1400	25-35	27.8
	Fe	1400	15-20	16.7
Lead Blast Furnace	Ca	1200	5	--
	Fe	1200	<38	8.8
	Ca	1400	10-20	25.2
	Fe	1400	<38	20.7

(1) Arsenic present as a mixture of arsenates and arsenites.

(2) Estimated content. The effect of minor constituents not considered.

(3) Experimental arsenic concentrations achieved to date, (these of course, are not equibibrium solubilities).

content. After the initial shake test, up to 180 hours, the samples are stored for aging. A data summary is presented in Table 40.

It should be noted and emphasized that the leach tests are based on complete immersion in the liquid leach solution. The system is also agitated. Actual plant storage of a solidified slag product will not require stability against either condition. Slag disposal will most likely consist of ladle transfer from the smelter to a storage area where the molten contents will be dumped (40 to 60 tons at a time). It will flow over previously dumped slag. The surface area exposed to weathering will, therefore, be minimal. In fact, if further protection from weathering were desired, each layer of arsenic containing slag could be covered by a layer of slag without arsenic. Also, the slag system in dry climates such as Montana and Arizona would not be exposed to much water leachate. Because of these differences, a series of outside column leach tests was made to simulate more appropriately the actual storage conditions.

Leach tests, (Table 40) were conducted for periods up to over 8000 hours. The arsenic content of the slag was varied from 0.3 percent to over 25 percent. As seen in Table 40, many slag matrices were used. The matrix showing the lowest percent arsenic extraction was clay, i.e., the extraction appears to have leveled off for the slags made from clay with iron arsenate added as the source of arsenic (Samples 30, 31, 32, and 63). The

TABLE 40. EXPERIMENTAL LEACH RESULTS FOR SLAG SOLVENTS

Sample No.	As Used (1)	Solvent	As Content of Prod. %	Arsenic Extraction							
				HRS.	%As	HRS	%As	HRS	%As	HRS	%As
1	Fe	B.F. Slag	(3) 9.7	43	0	403	0.015	1128	0.012	2040	0.015
2	Fe	B.F. Slag	8.4	43	0	403	0.020	1128	0.018	2112	0.021
3	None	B.F. Slag	0.3	43	0	403	0.016	1128	0.033	2112	0.090
4	Fe	B.F. Slag	9.7	43	0	403	0.027	1128	0.026	2112	0.030
6	Fe	B.F. Slag	8.1	43	0	403	0.021	1128	0.010	2040	0.007
52	Fe	B.F. Slag	9.1	43	0.016	600	0.042	1587	0.071	-	-
53	Fe	B.F. Slag	20.7	43	0.018	600	0.056	1587	0.081	-	-
54	Fe	B.F. Slag	8.8	43	0.018	600	0.056	1587	0.081	-	-
12	Ca	B.F. Slag	13.7	43	0.018	403	0.012	1128	0.012	2112	0.012
13	Ca	B.F. Slag	18.6	43	0.021	403	0.035	1128	0.035	2115	0.059
15	Ca	B.F. Slag	12.4	43	0.023	403	0.024	1104	0.008	2000	0.007
16	Ca	B.F. Slag	25.2	43	0	403	0.006	1104	0.013	2040	0.005
17	Ca	B.F. Slag	16.4	43	0	403	0.006	1104	0.008	2091	0.004
18	Ca	B.F. Slag	18.2	43	0.016	382	0.005	1104	0.009	2091	0.020
29	Ca	B.F. Slag	16.4	43	0.002	160	0	859	0.014	1771	0.016
59	Ca	B.F. Slag	16.6	43	0.044	264	0.105	-	-	-	-
11	None	R. Slag	(4) 0.8	43		403	0	1128	0.013	2112	0
5	Fe	R. Slag	12.9	43	0.004	403	0.242	1128	0.271	2112	0.558
7	Fe	R. Slag	4.5	43	0.056	403	-	1128	0.044	2112	0.044
27	Fe	R. Slag	8.8	43	0.004	160	0	859	0.007	1846	0
28	Fe	R. Slag	8.8	43	0.014	859	0.027	1846	0.022	-	-
9	Ca	R. Slag	13.5	43	0.010	403	0.013	1128	0.016	2112	0.050
10	Ca	R. Slag	19.5	43	0	403	0.006	1128	0.012	2040	0.021
20	Ca	R. Slag	17.4	43	0	382	0.011	2091	0.014	-	-
21	Ca	R. Slag	13.4	43	0	0	0	2091	0.010	-	-
58	Ca	R. Slag	18.4	43	0.013	264	0.019	1251	0.022	-	-
60	Ca	R. Slag	23.5	43	0.012	264	0.019	1172	0.037	-	-
41	Fe	P. Slag (5)	12.2	43	0.005	600	0.024	1587	0.017	-	-
43	Fe	P. Slag	9.7	43	-	160	0	600	0.033	1587	0.050
44	Ca	P. Slag	12.9	43	0.016	160	0.027	600	0.046	1587	0.087
49	Ca	P. Slag	7.2	43	0.115	160	0.243	600	0.236	1587	0.324

NOTE: % DATA FOR LONGER LEACH TIMES CONTINUED ON PAGE 103

(continued)

TABLE 40 (continued)

		(6)									
38	Fe	P. Rock	7.1	43	0	160	0.011	859	0.020	1846	0.015
56	Fe	P. Rock	8.6	43	0.006	264	0.006	1176	0.009	-	-
		(7)									
36	Fe	Ash	8.6	43	0.005	859	0.005	1846	0.00	-	-
47	Fe	Ash	12.3	43	0.002	403	0.028	600	0.179	1587	0.003
61	Fe	Ash	20.9	43	0.013	264	0.003	1251	0.006	-	-
62	Fe	Ash	13.5	43	0.012	264	0.002	1251	0.036	-	-
37	Ca	Ash	14.0	43	0.001	160	0.001	859	0.007	1846	0.005
48	Ca	Ash	18.7	43	0.025	600	0.005	1587	0.004	-	-
50	Ca	Ash	17.4	43	-	160	0.014	1587	0.014	-	-
		(8)									
30	Fe	Clay	9.4	43	0	859	0.004	1846	0	-	-
31	Fe	Clay	17.2	43	0	160	0.003	1846	0.002	-	-
32	Fe	Clay	11.4	43	0	160	0	1846	0.006	-	-
63	Fe	Clay	16.0	43	0.001	264	0.010	1251	0.003	-	-
19	Ca	Clay	17.1	43	0	1104	0.006	2091	0.002	-	-
51	Ca	Clay	19.5	43	0.225	600	0.662	1587	1.327	-	-
		(9)									
35	Fe	Dust	12.9	43	0.023	859	0.046	1846	0.042	-	-
46	Fe	Dust	16.1	43	0.027	160	0.044	600	0.038	1587	0.097
33	Fe,Ca	R. Slag	10.6	43	0.024	859	0.062	1846	0.044	-	-
39	Fe	B. F. Slag									
		P. Rock	7.9	43	0	403	0	859	0.015	1846	0.009
40	Ca	P. Rock	6.6	43	0	403	0	859	0.004	1846	0.002
		(10)									
14	Ca	N. Slag	14.4	43	0.149	403	0.417	-	-	-	-
22	Ca	N. Slag	24.1	43	0.052	382	0.234	-	-	-	-

NOTE: % DATA FOR LONGER LEACH TIMES CONTINUED ON PAGE 104

(1) Mixture of arsenates and arsenites
(2) Starting solution pH's ranged from 5.7 to 5.9
(3) Lead blast furnace slag
(4) Copper reverberatory slag
(5) Phosphorus production slag
(6) Phosphorus containing slag
(7) Coal Fired power generating plant ash
(8) Bentonite
(9) Cement Plant cottrell dust
(10) Sodium silicate slag

For a solid liquid ratio of 1:100, the As concentration in the leach solution can be calculated by multiplying column 4 times %As extraction. This calculation gives the concentration in ppm.

TABLE 40 (continued)

Sample No.	Arsenate Used (1)	Solvent	As Content of Prod. %	Arsenic Extraction			
				HRS.	%As	HRS.	%As
1	Fe	B. F. Slag (3)	9.7	6792	0.022	8304	0.019
2	Fe	B. F. Slag	8.4	6792	0.048	8304	0.057
3	None	B. F. Slag	0.3	6792	0.067	8304	0.10
4	Fe	B. F. Slag	9.7	6792	0.039	8304	0.082
6	Fe	B. F. Slag	8.1	6792	0.028	8304	0.022
52	Fe	B. F. Slag	9.1	6480	0.110	7992	0.165
53	Fe	B. F. Slag	20.7	6480	0.056	7992	0.097
54	Fe	B. F. Slag	8.8	6480	0.153	7992	0.205
12	Ca	B. F. Slag	13.7	6792	0.032	8304	0.088
13	Ca	B. F. Slag	18.6	6792	0.180	8304	0.215
14	Ca	B. F. Slag	12.4	6480	0.039	7992	0.021
15	Ca	B. F. Slag	25.2	6480	0.012	7992	0.013
17	Ca	B. F. Slag	16.4	6480	0.030	7992	0.061
18	Ca	B. F. Slag	18.2	6480	0.087	7992	0.121
29	Ca	B. F. Slag	16.4	6432	0.033	7944	0.031
59	Ca	B. F. Slag	16.6	5640	0.167	7152	0.386
11	None	R. Slag (4)	0.8	6792	0.038	8304	<0.047
5	Fe	R. Slag	12.9	6792	1.02	8304	0.021
7	Fe	R. Slag	4.5	6792	0.151	8304	0.222
27	Fe	R. Slag	8.8	6432	0.023	7944	0.004
28	Ca	R. Slag	8.8	6432	0.063	7944	0.055
9	Ca	R. Slag	13.5	6792	0.027	8309	0.016
10	Ca	R. Slag	19.5	6792	0.031	8309	0.062
20	Ca	R. Slag	17.4	6480	0.037	7992	0.126
21	Ca	R. Slag	13.4	6480	0.017	7992	0.13
58	Ca	R. Slag	18.4	5640	0.051	7152	0.098
60	Ca	R. Slag	23.5	5640	0.046	7152	0.094
41	Fe	P. Slag (5)	12.2	6288	0.039	7800	0.036
43	Fe	P. Slag	9.7	6288	0.023	7800	0.144
42	Ca	P. Slag	13.7	5976	0.102	7988	0.102
44	Ca	P. Slag	12.9	5976	0.279	7988	0.600
49	Ca	P. Slag	7.2	5976	0.472	7488	1.46

TABLE 40 (continued)

Sample No.	Arsenate (1) Used	Solvent	As Content of Prod. %	Arsenic Extraction			
				HRS.	%As	HRS.	%As
38	Fe	P. Rock (3)	7.1	6288	0.033	7800	0.031
56	Fe	P. Rock	8.6	5649	0.021	7152	0.021
36	Fe	Ash	8.6	6288	0.006	7800	0.004
47	Fe	Ash	12.3	5976	0.002	7488	0.003
61	Fe	Ash	20.9	5640	0.026	7152	0.023
62	Fe	Ash	13.5	5640	0.069	7152	0.119
37	Ca	Ash	14.0	6288	0.021	7800	0.016
48	Ca	Ash	18.7	5976	0.012	7488	0.14
50	Ca	Ash	17.4	5976	0.030	7488	0.057
30	Fe	Clay	9.4	6408	0.005	7920	0.004
31	Fe	Clay	17.2	6336	0.002	7848	0.002
32	Fe	Clay	11.4	6312	0.004	7824	0.003
63	Fe	Clay	16.0	5640	0.002	7152	0.002
19	Ca	Clay	17.1	6480	0.021	7992	0.010
51	Ca	Clay	19.5	5976	1.54	7988	3.59
35	Fe	Dust	12.9	6288	0.123	7800	0.140
46	Fe	Dust	16.1	6288	0.152	7800	--
33	Fe,Ca	R. Slag	10.6	6312	0.103	7829	0.132
39	Fe	B. F. Slag P. Rock	7.9	6288	0.033	7800	0.14
40	Ca	P. Rock	6.6	6288	0.021	7800	0.006
14	Ca	N. Slag	14.4				
22	Ca	N. Slag	24.1				

extraction percent after about 7800 hours is the same as measured after about 1800 hours, i.e., approximately 0.002 to .004 percent (0.03 ppm extracted after 325 days).

Even though the clay matrix samples appear to be the most stable (to water leaching) of the slag products, it is important to remember that from an economic and energy conservation standpoint, the use of molten smelter slag is a more desirable solvent, i.e., the molten solvent is readily available at the smelter site. The leach results are somewhat variable for the reverberatory slag and the lead blast furnace slags, but in general, the percent extraction for the longer term tests is less than 0.1 percent (1 ppm extracted). It can also be seen that the general trend is that arsenic extraction has not leveled off with time as was the case for the clay slag matrix samples.

Samples 16, 27, 39, and 51 were chosen for metallographic preparation and observation. The results showed a glassy structure, i.e., there was no evidence of non-solution of the arsenate phase (Figure 12). Evidently the experimental rate of cooling was sufficiently rapid to retain the glassy phase without precipitation of a second phase. There was one exception to this, i.e., some second phase precipitation occurred in the iron arsenate-phosphorus rock-blast furnace slag mixture (Sample 39), Figure 13. The second phase concentration is estimated to cover only about five percent of the examined surface. The presence of

Fig 12

F-13

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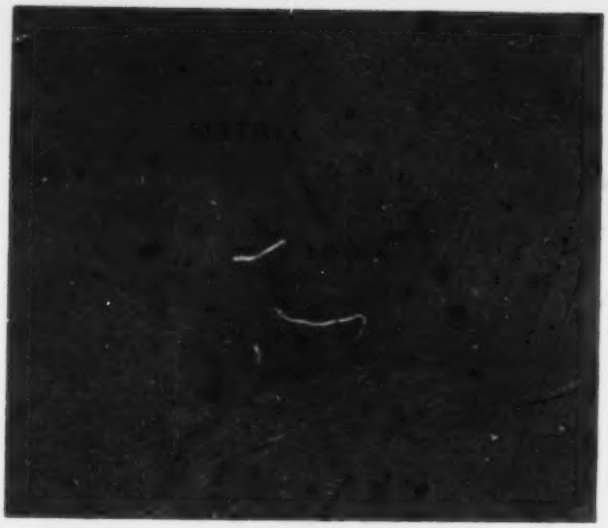

Figure 12. Typical slag product.

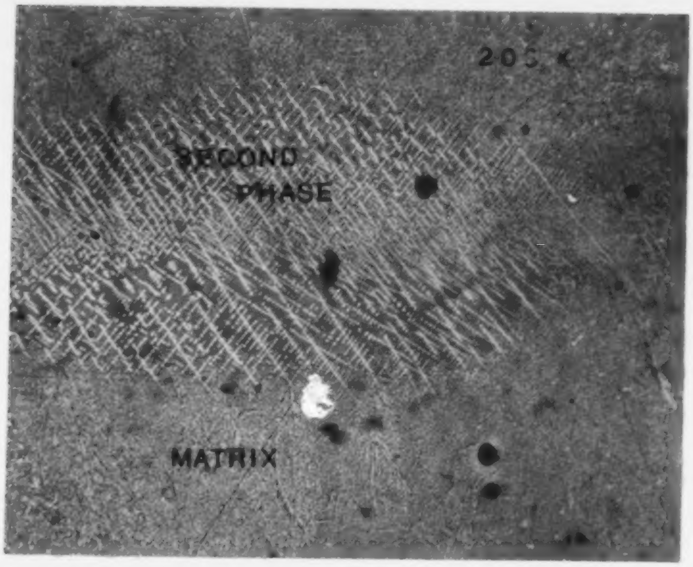

Figure 13. Second phase precipitation

a duplex structure is not necessarily bad, i.e., it may not enhance the arsenic leach rate.

A series of arsenic containing slags was slow cooled to intentionally precipitate phases within the glass matrix. The purpose was to investigate how the arsenic would behave in a slow-cooled system, i.e., would it remain predominately in the glass structure or would it be precipitated as a second phase in the slag matrix?

Slag-arsenate mixtures were melted at 1300° to 1400°C. The samples were then held for one hour at successively lower temperatures in 50°C increments to 800°C, then held at this temperature overnight (about 15 hours). Photomicrographs of the results are shown in Figures 14 though 19.

Leach tests on the slow cooled samples (Table 41) have been conducted for up to 6480 hours. Scanning Electron Microscopy technique was used to study the distribution of arsenic in the slag samples that were prepared by dissolving iron arsenate in the copper smelter reverberatory slag and lead blast furnace slag.

T41

Three samples were looked at. Sample Number 76 which was obtained by dissolving iron arsenate into the reverberatory slag with the final arsenic concentration of 8.5 percent. Sample Number 77 is the same as Number 76, except the arsenic concentration is 19.8 percent. The third sample (Number 78) was obtained by dissolving iron arsenate into the lead blast furnace slag with arsenic concentration at 13.3 percent.

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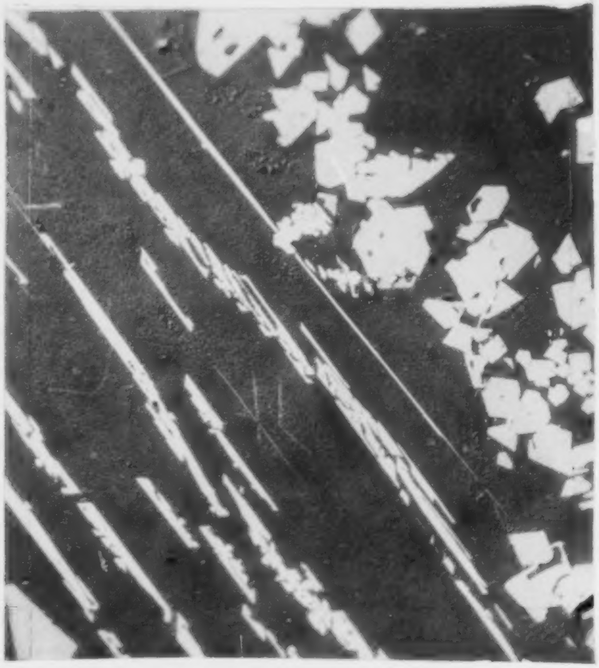

Figure 14. Reverberatory slag: iron arsenate used as arsenic carrying compound added to molten slag.

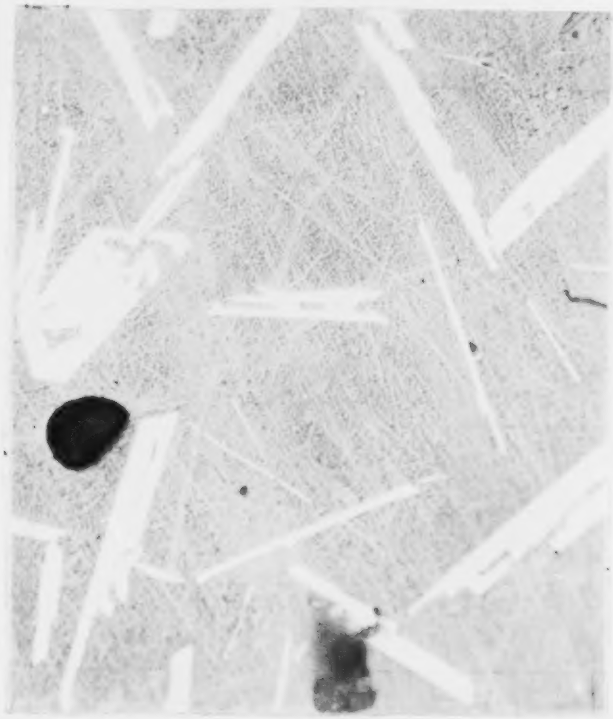

Figure 15. Reverberatory slag: iron arsenate used as arsenic carrying compound added to molten slag.

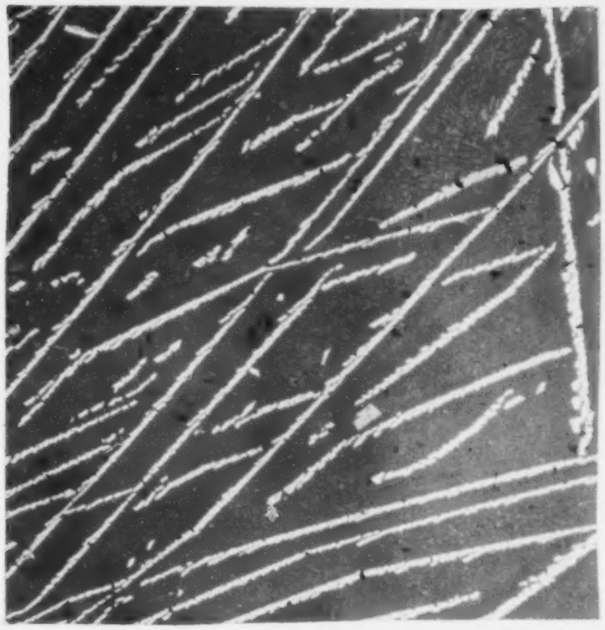

Figure 16. Lead blast furnace slag: iron arsenate used as arsenic carrying compound added to molten slag.

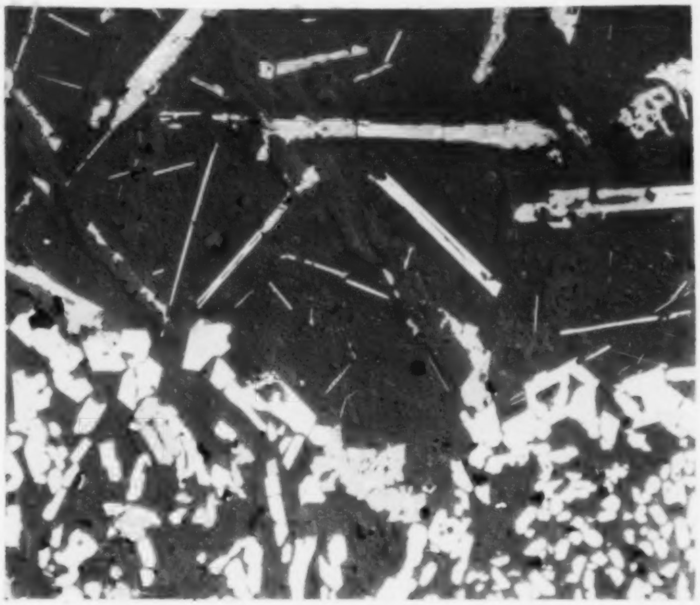

Figure 17. Lead blast furnace slag: calcium arsenate used as arsenic carrying compound added to molten slag.

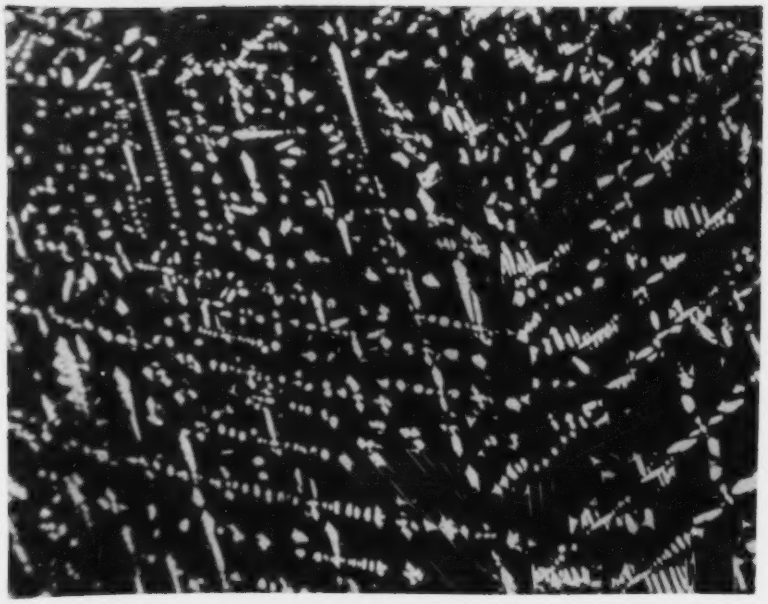

Figure 18. Bentonite clay: iron arsenate used as arsenic carrying compound added to molten solvent.

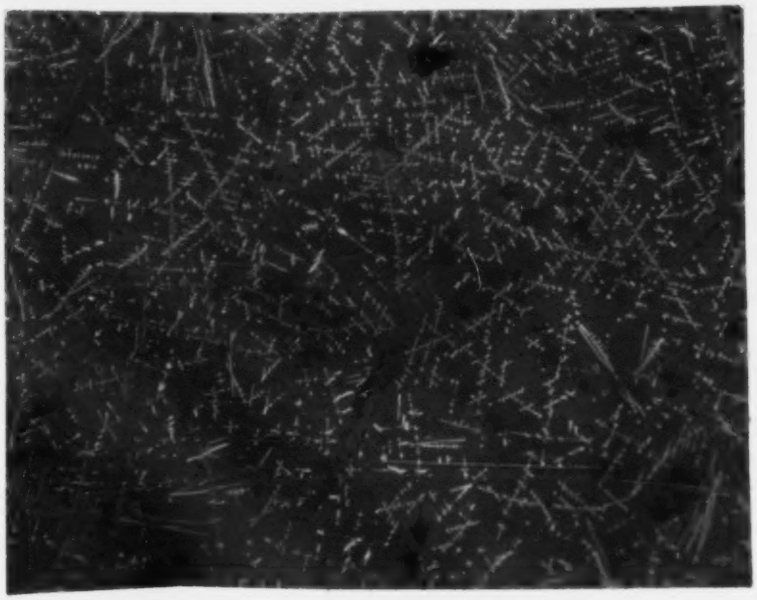

Figure 19. Power plant fly ash: iron arsenate used as arsenic carrying compound added to molten solvent.

TABLE 41. LEACH TESTS ON SLOW COOLED ARSENIC CONTAINING SLAGS

Sample No.	Arsenate Used	Solvent	% Arsenic in Product	HRS.	Arsenic Extraction %	HRS.	Arsenic Extraction	HRS	As Ext.%	HRS	As Ext. %
69	Fe	Clay	16.8	1	0.009	531	0.002	4968	0.002	6480	.004
70	Fe	Ash	7.0	1	0	456	0.014	4968	.043	6480	.0.37
71	Ca	Blast Furnace	13.8	1	0.001	456	0.030	4968	0.30	6480	0.38
76	Fe	Reverberatory Slag	8.5	1	0	456	0.006	4968	0.014	6480	0.013
77	Fe	Reverberatory Slag	19.8	1	0.002	531	0.014	4968	0.028	6480	0.0[illegible]
78	Fe	Blast Furnace Slag	13.3	1	0.001	456	0.038	4968	0.15	6430	0.23

Explanatory notes are given with all the photomicrographs and the dot-maps. For each sample, conclusions are presented at the end of the particular picture series.

Sample 76 Reverberatory Slag (8.5 Percent As)

A photomicrograph is presented in Figure 20. Note the presence of several phases. Elemental distribution of Zn, As, Si, and Fe is presented in Figures 20 through 24.

Iron arsenate dissolved completely in the lead blast furnace slag. Arsenic appears to be concentrated in the matrix rather than in the associated precipitated phases that form during slow cooling.

Zinc and silicon are also concentrated in the matrix phase rather than the large precipitated phase. Iron occurs primarily in the precipitated phase.

Sample 77 Reverberatory Slag (19.8 percent As)

A photomicrograph is presented in Figure 25. Elemental distribution is presented in Figures 26 through 28.

This sample is similar to Sample 76, i.e., it was made by dissolving iron arsenate in copper reverberatory slag. The difference is the arsenic content; Sample 76 contains 8.5 percent As and Sample 77 contains 19.8 percent As.

Arsenic in both Samples 76 and 77 appears to be concentrated in the slag matrix rather than in precipitated phases. The distribution of iron and silicon is the same as quoted for Sample

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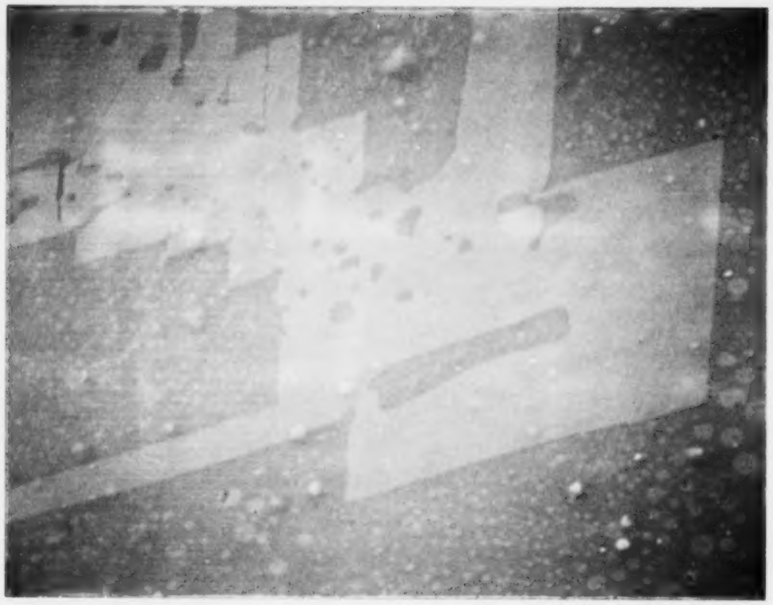


Figure 20. Iron arsenate dissolved in reverberatory slag - slow cooled (Sample 76).

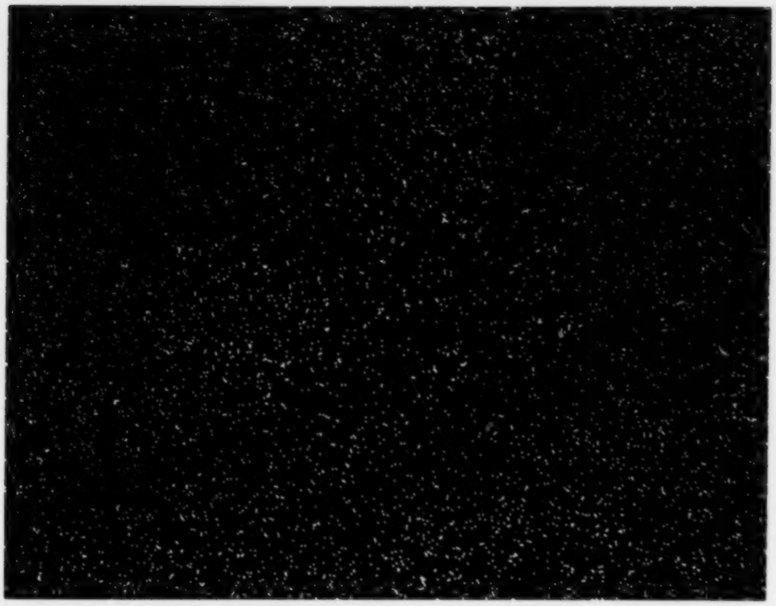


Figure 21. Dot map for zinc distribution in Sample 76.

Note that if this map is superimposed over the photomicrograph (Figure 20) that the major distribution of zinc lies outside the larger precipitated phase.

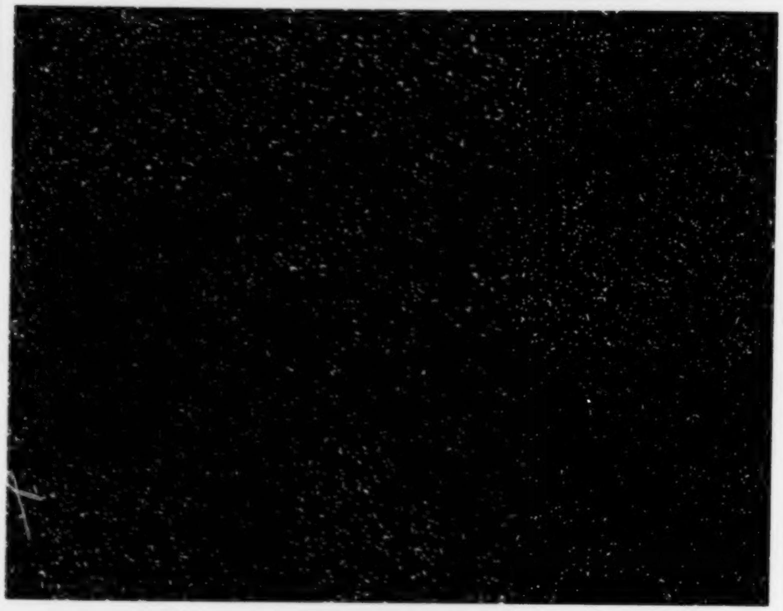
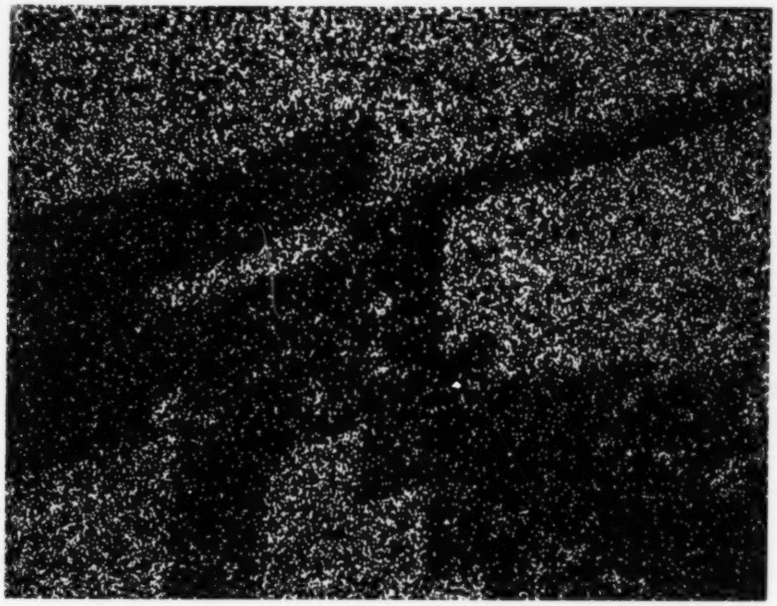


Figure 22. Dot map for arsenic distribution in Sample 76.

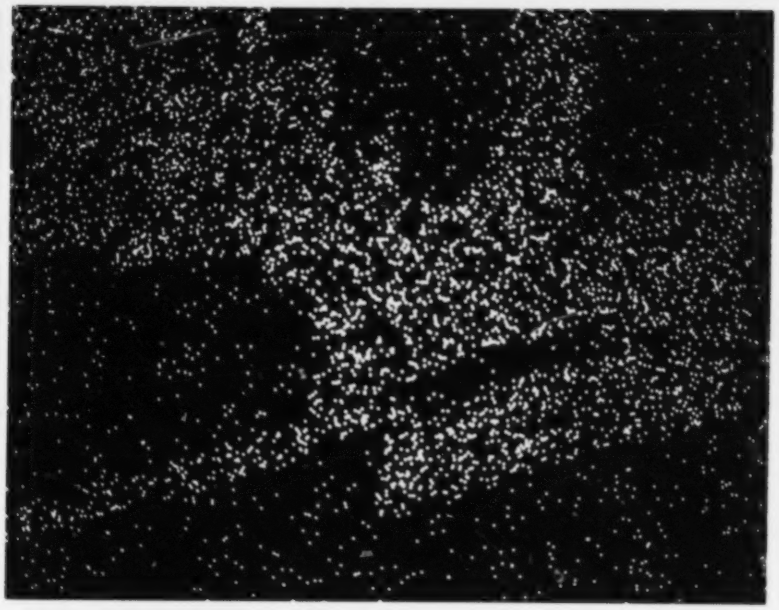
Arsenic intensity is low but the map shows that the large precipitated phase does not contain the major amount of arsenic.



1000 X

Figure 23. Dot map for silicon distribution in Sample 76.

Note that silicon occurs primarily in the background, i.e., it does not concentrate in the large precipitated phase. It lies mainly in the matrix.

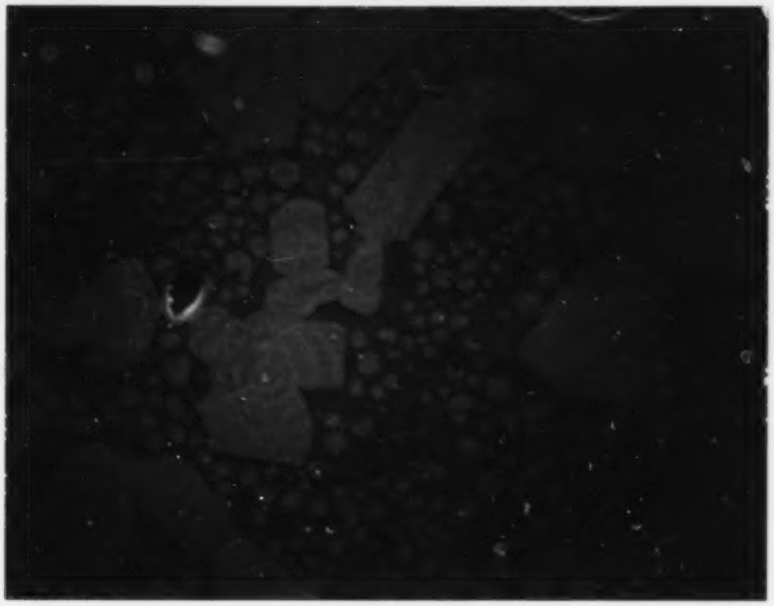


1000 X

8.5% As

Figure 24. Dot map for iron distribution in Sample 76.

Note that iron occurs predominantly in the large precipitated phase.



19.8% As

1000 X

Figure 25. Iron arsenate dissolved in copper reverberatory slag - slow cooled Sample 77.

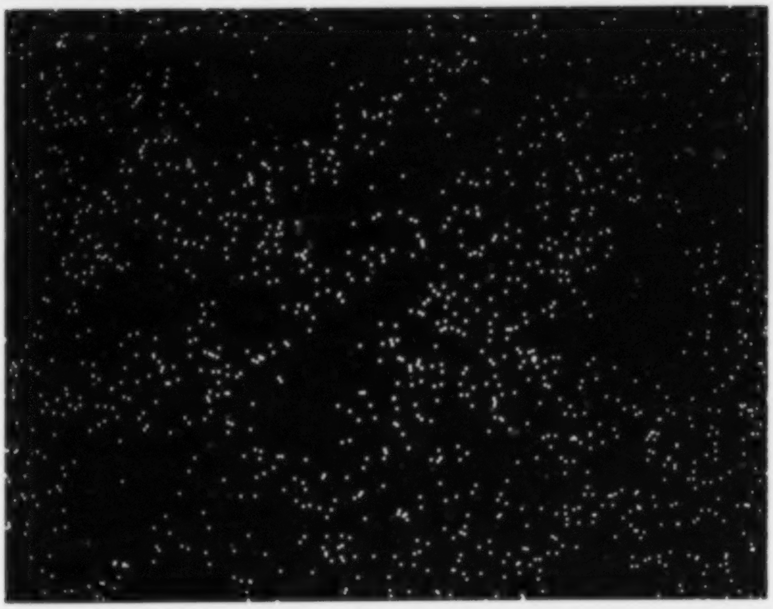

1000 X

Figure 26. Dot map for arsenic distribution in Sample 77.

Note that if this map is superimposed on the photomicrograph (Figure 25), arsenic is not present in the large precipitated phase.

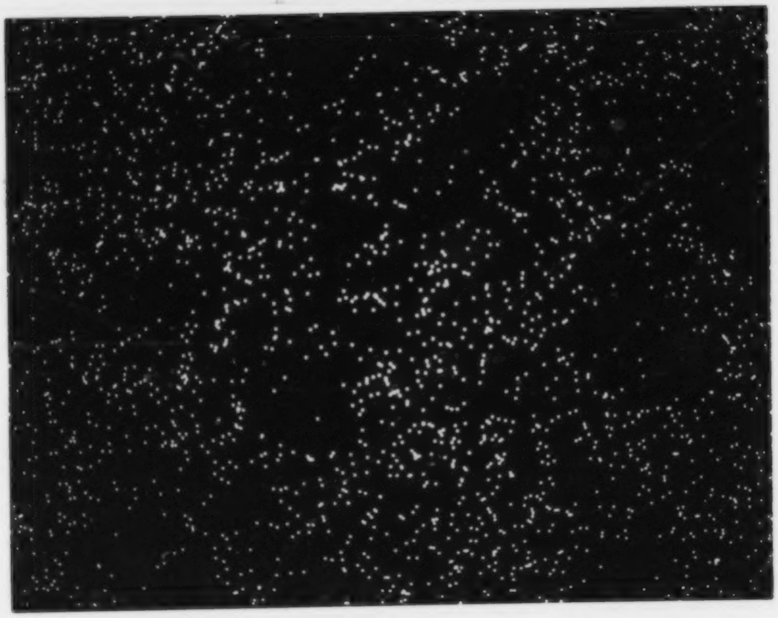
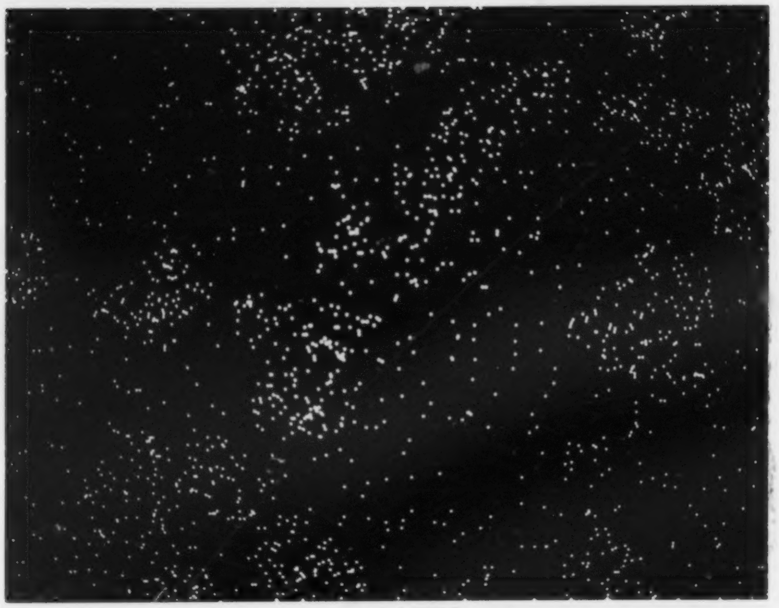


Figure 27. Dot map for silicon distribution in Sample 77.

Note that if this map is superimposed on the 1000 X photomicrograph (Figure 25), silicon is primarily present in areas other than the large precipitated phase.



1000 X

Figure 28. Dot map for iron distribution in Sample 77.

Note that if this map is superimposed on the photomicrograph (Figure 25), iron is primarily present in the large precipitated phase.

76, i.e., silicon is present in the matrix, the iron is present in the large precipitated phase.

Sample 78 Lead Blast Furnace Slag (13.3 percent As)

Photomicrographs are presented in Figures 29, 34, and 37. Elemental distributions are presented in Figures 30 through 33, 35, 36, and 38 through 41.

Iron arsenate dissolved completely in the slag. Arsenic occurs in two forms when the slag is slow-cooled, i.e., it remains dissolved in the glass matrix and a portion associates with calcium and precipitates in crystalline form.

Silicon is almost totally present in the matrix, as is also Zn and Al.

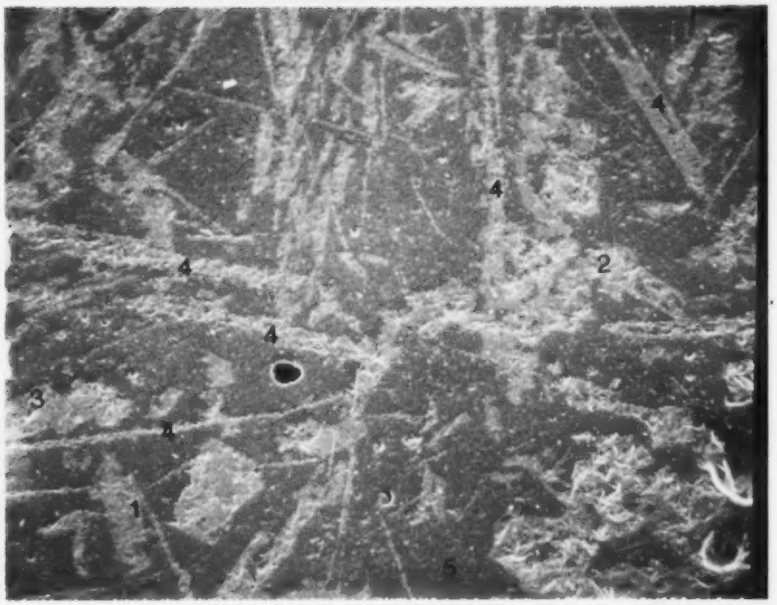
Iron precipitates as long needles. It is not associated with As, Zn, Al, Si, or Ca. What the compound of iron is has not been determined.

Lead blast furnace slag contains much greater calcium content than does reverberatory slag. This probably accounts for the formation of Ca and As together, which did not occur in the reverberatory slag sample studied previously. In fact, in that study it appeared that the arsenic was almost completely in the matrix, i.e., no precipitated phase high in arsenic formed.

Influence of Leach Variables--

Prior Surface Treatment--

Surface treatments prior to leaching appear to result in a decrease in the leach solution arsenic extraction for most cases;



13.3% As

1000 X

Figure 29. Iron arsenate dissolved in lead blast furnace slag - slow cooled Sample 78.

100 X

Figure 30. Dot map for arsenic distribution in Sample 78.

Note: Superimpose this map over the photomicrograph in Figure 29. Arsenic is concentrated in only a portion of the precipitated phases.

Figure 31. Dot map for iron distribution in Sample 78.

Note: Superimpose this map over the photomicrograph in Figure 29. Iron is concentrated in the long needle-like crystals (Area 4 in Figure 29). This was verified by analysis of the spectrum emitted from the needles. Iron is not associated with the high arsenic phase.

Figure 32. Dot map for calcium distribution in Sample 78.

Note: Calcium is associated with the arsenic rich phase (Areas 1, 2, and 3 of Figure 29). It is also present in other precipitated phases. It is not present in the iron rich phase.

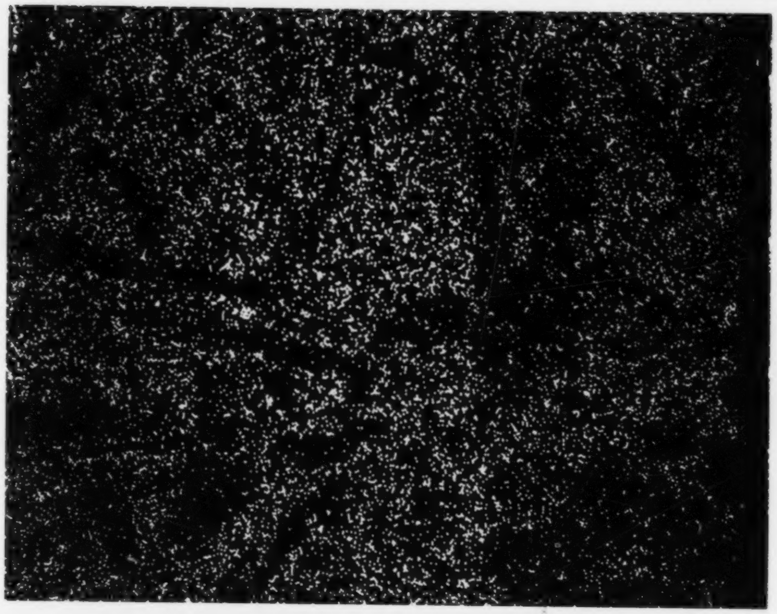


Figure 33. Dot map for silicon distribution in Sample 78.

Note: Silicon is present mainly in the matrix. Areas 1, 2, 3, and 4 of Figure 29 show a deficiency of silicon compared to the glass matrix (the grey areas in Figure 29).

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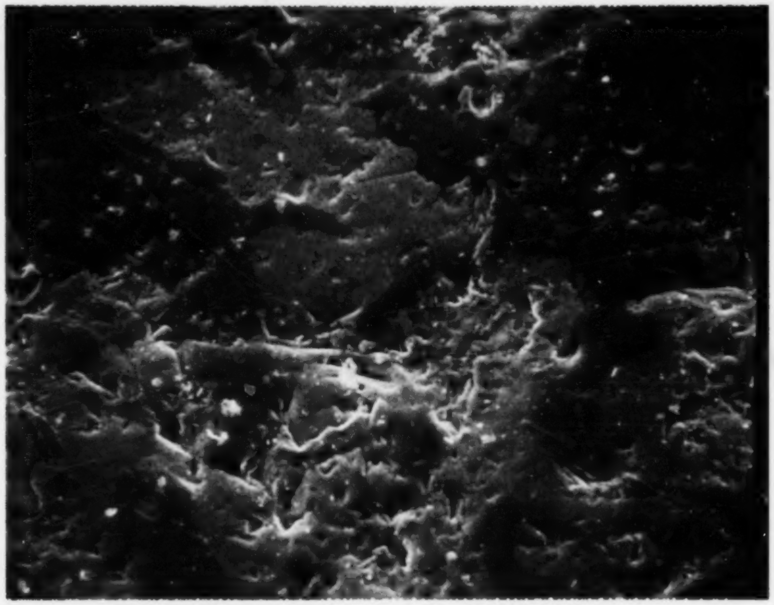
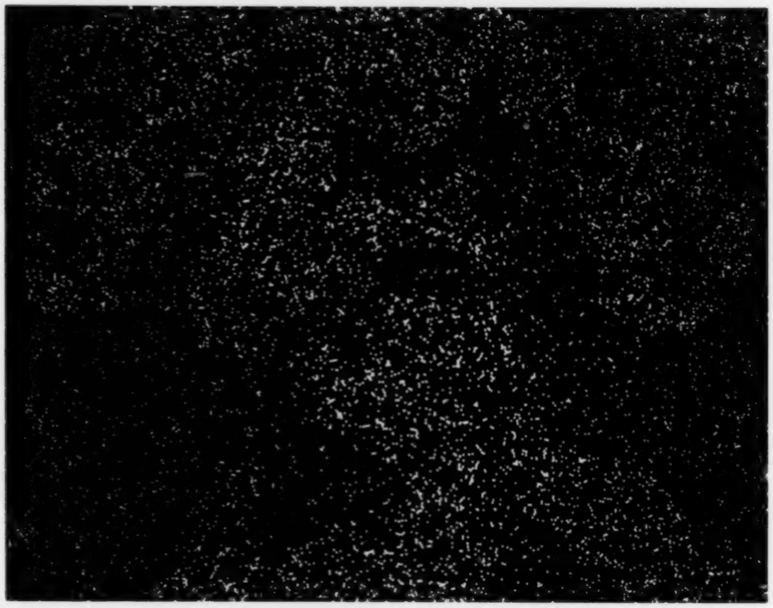


Figure 34. Sample 78, Area 2 of Figure 29, magnified to 700 X.

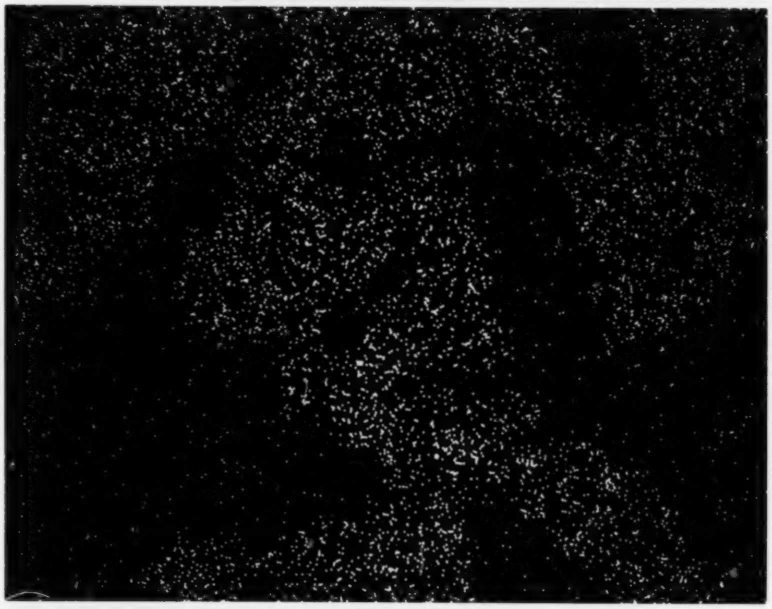
Note: This area was shown to be a high arsenic, high calcium, low iron, low silicon phase. Dot maps follow in Figures 35 and 36 for Ca and As.



700 X

Figure 35. Dot map for arsenic distribution in Area 2 of Sample 78.

Note: The arsenic appears to be concentrated in the lighter grey areas of Figure 34. This is true also of calcium (Figure 36). Therefore, arsenic and calcium occur together.



700 X

Figure 36. Dot map for calcium distribution in Area 2 of Sample 78.

Note: Calcium is definitely concentrated in the lighter grey areas of the precipitated phase.

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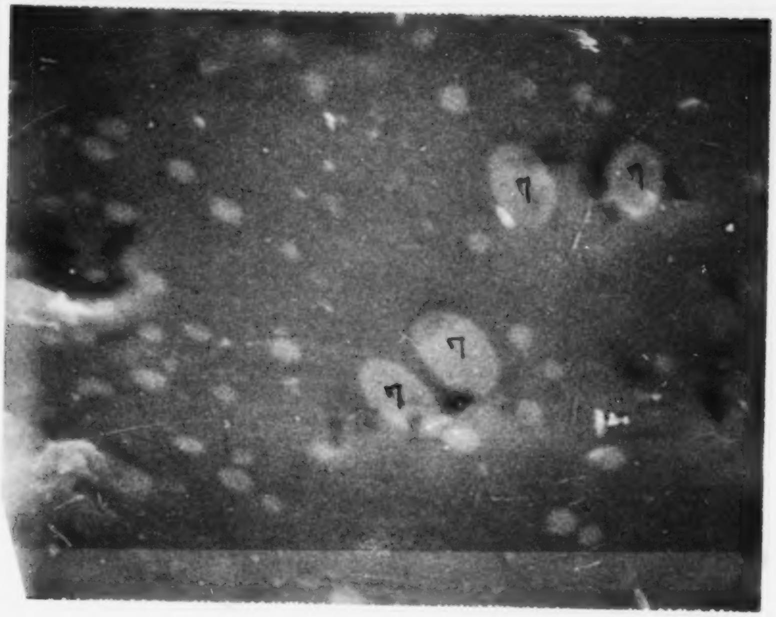
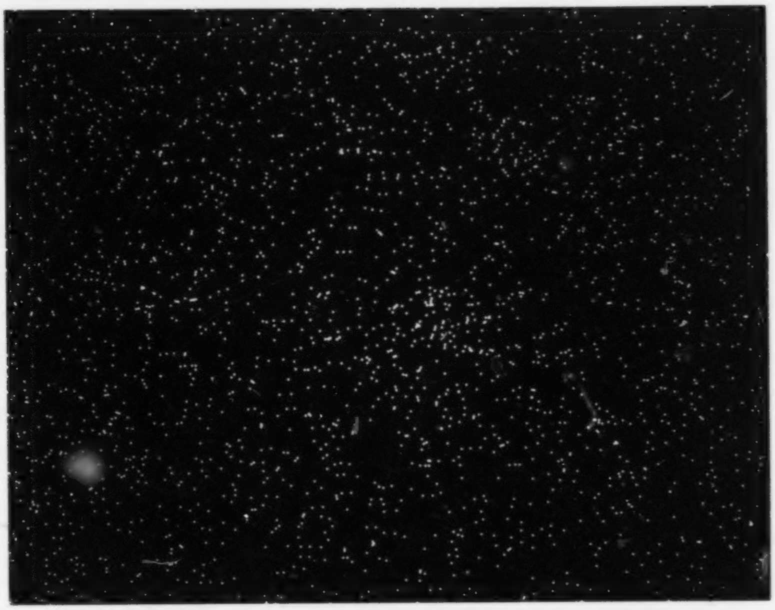


5000 X

Figure 37. Sample 78, Area 5 of Figure 5, magnified to 5000 X.

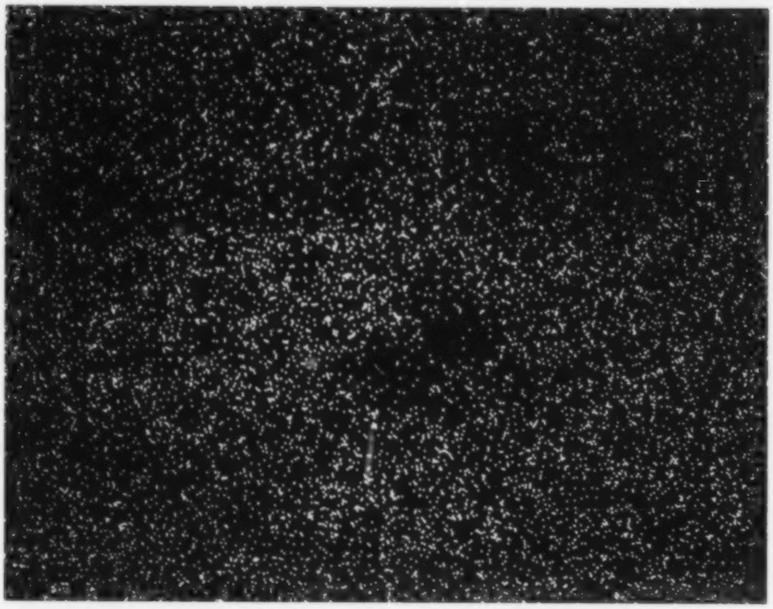
Note: Matrix is actually made up of a grey background (presumably the glass solvent) and precipitated light grey areas (Number 7) on this photomicrograph. The area shown above is low in calcium and iron, high in silicon, zinc, aluminum, and arsenic.



5000 X

Figure 38. Dot map for arsenic distribution in Matrix Area 7.

Note: Arsenic is not concentrated in the precipitated phase. It is high in the glass matrix (this conclusion is drawn from spectra data collected for this region of the sample). Therefore, in Sample 78, arsenic is both in the matrix and also in one of the precipitated phases.



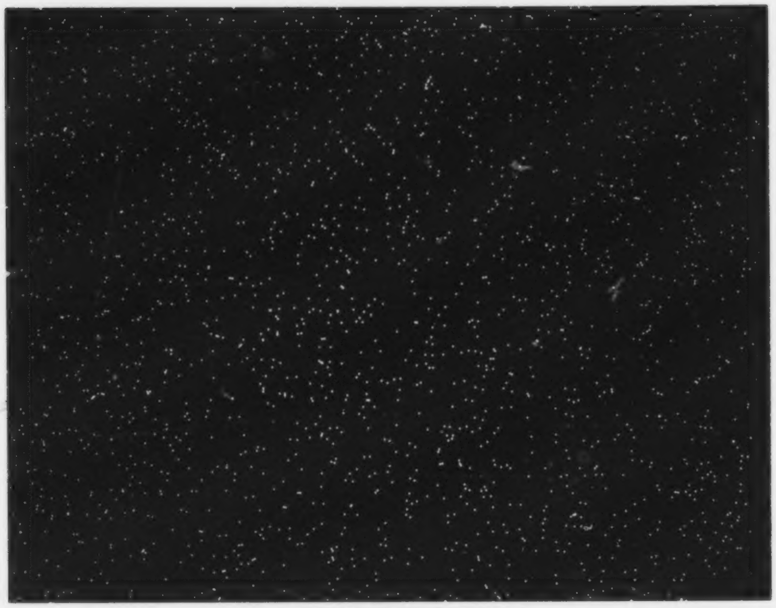
5000 X

Figure 39. Dot map for silicon distribution in Matrix Area 5.

Note: The background matrix is high in silicon, the round precipitated phase is lower in silicon. The presence of silicon in the matrix phase is in agreement with the earlier data.

Figure 40. Dot map for aluminum distribution in Matrix Area 5.

Note: Aluminum is primarily present in the matrix area.



5000 X

Figure 41. Dot map for zinc distribution in Matrix Area 5.

Note: Zinc is present primarily in the matrix phase.

for comparative results see Table 42. Both hot water and dilute (pH = 2) sulfuric acid treatment of the slag particles were performed on selected samples. The desired result was to remove any surface contamination picked up during handling of the samples and to, perhaps, leach surface arsenic from the structure. T-42

Solid-Liquid Ratio--

The influence of solid-liquid ratio, and the effect of surface area were studied. Samples of each of four slag systems were pulverized and screened to -100 mesh particle size. These samples were then leached at solid:liquid ratios of 1:100, 1:10, 1:1 in distilled water was described earlier. The results are reported in Table 43. So, when the solid:liquid ratio was increased, the concentration of arsenic in the liquid phase increased, e.g., for Samples 117 through 119 (reverberatory slag containing 8.9 percent As) after 5880 hours, the concentrations were 11 ppm (1:100), 63 ppm (1:10), and 95 ppm (1:1). However, the percent arsenic extracted from the solids was less for the 1:1 ratio than for the 1:100 ratio. T-43

Particle Size--

The influence of starting sample particle size at a fixed solid:liquid ratio was investigated for the four slag systems. Three size fractions were prepared, i.e., 1/4 inch pieces, -8/+10 mesh, -60/+100 mesh. These samples were leached in solid: liquid ratios of 1:1, 1:10, 1:100. The starting solution was distilled water, pH ≈5.7. The pH of the solution was not con-

TABLE 42. PRIOR SURFACE TREATMENT

Sample Number		Extraction		Results					
		HRS	%	HRS	%	HRS	%	HRS	%
84	Hot water leach of sample number 6	1	0	472	0.009	4968	0.009	6480	0.019
6	Untreated			2040	0.007	-	-	6792	0.028
85	Hot water leach of sample number 27	1	0	472	0.002	4968	0.004	6480	0.004
27	Untreated	859	0.007	1846	0	-	-	6432	0.023
86	Hot water leach of sample number 56	1	0.002	472	0.001	4968	0.008	6480	0.008
56	Untreated	264	0.006	1176	0.009	-	-	7152	0.021
87	Hot water leach of sample 62	1	0.001	472	0.035	4968	0.07	6480	0.09
62	Untreated	264	0.002	1251	0.036	-	-	7152	0.119
88	Hot water leach of sample #32	1	0	472	0.001	6480	<0.003		
32	Untreated	160	0	1846	0.006	6312	0.004		
89	Hot water leach of sample 40	1	0.003	531	0	6480	<0.006		

(continued)

TABLE 42 (continued)

40	Untreated	859	0.015	1846	0.009	6288	0.021
90	Hot water leach of sample 53	1	0.001	472	0.013	4968	0.033
53	Untreated	600	0.046	1587	0.056	6480	0.056
93	Hot water leach of sample 10	1	0.002	531	0.036	6480	0.056
10	Untreated	1128	0.012	2040	0.021	6792	0.031
96	Hot water leach of sample 50	1	0.001	531	0.015	6480	0.069
50	Untreated	160	0.014	1587	0.014	5976	0.030
91	Hot water leach of sample 16	1	0.001	472	0.009	6480	0.040
92	Acid leach of sample 16	1	0.009	472	0.010	6480	<0.001
16	Untreated	1104	0.013	204	0.005	6480	0.012
94	Hot water leach of sample 60	1	0.002	472	0.005	6480	0.026
95	Acid leach of sample 60	1	0.001	531	0.006	6480	0.063
60	Untreated	264	0.019	1172	0.037	7152	0.094

TABLE 43. INFLUENCE OF SOLID:LIQUID RATIO ON ARSENIC EXTRACTION
(minus 100 mesh solids)

Sample No.	Slag System	Arsenate(1) Source	S/L Ratio	Per cent 1 Hr	Arsenic 288 Hr	Extracted 5880 Hr
117	Reverberatory Slag (8.9 %As)	$FeAsO_4$	1:100	0.05	0.05	0.35
118		$FeAsO_4$	1:10	0.20	0.02	0.18
119		FeAsO4	1:1	-	0.01	0.11
123	Reverberatory Slag (12.9 %As)	$Ca_3(AsO_4)_2$	1:100	0	0.02	0.16
124		$Ca_3(AsO_4)_2$	1:10	0.23	0.01	0.08
125		$Ca_3(AsO_4)_2$	1:1	-	-	-
114	Blast Furnace Slag (10.2 %As)	FeAsO4	1:100	0	0.13	1.07
115		$FeAsO_4$	1:10	0.19	0.03	0.62
116		FeAsO4	1:1	0.08	0.01	0.09
120	Blast Furnace Slag (15.6 %As)	$Ca_3(AsO_4)_2$	1:100	-	0.06	1.28
121		$Ca_3(AsO_4)_2$	1:10	-	0.02	0.26
122		$Ca_3(AsO_4)_2$	1:1	-	<0.005	0.06

(1) The arsenate shown was used as the carrier for dissolution in the molten solvent slag.

trolled. It varied according to the local conditions in each test sample system.

T 44-47

The leach results are reported in Tables 44 through 47 for test periods up to 2300 hours. The test period has not been sufficiently long to draw conclusions concerning long term leach effects, but one can note some generalities occurring in the present data through 2300 hours of testing. The arsenic extraction does appear to be a function of particle size. The observation is, as would be expected, that the arsenic released to the solution does occur at a faster rate for the smaller particle size samples, i.e., more surface area is available for the leach reaction to occur. The reverberatory slag (prepared using iron arsenate as the arsenic carrier) showed (Table 44) about twice the percent extraction for the -60/+100 fractions over the 1/4-inch sample. The trend is not as clear cut for the data presented in Table 45 for the reverberatory slag prepared using calcium arsenate as the arsenic carrier. The 2300 hour data appear to suggest no effect or even a reverse effect with respect to particle size.

The lead blast furnace slags show leach results that agree with the trend of extraction doubling (2300 hours) for the -60/+100 size fraction over the 1/4-inch samples (Tables 45 and 46).

Acidity--

The influence of controlling the pH of the leach solution was studied. The solid:liquid ratio was maintained at 1:100 for

TABLE 44. INFLUENCE OF PARTICLE SIZE ON ARSENIC EXTRACTION FROM REVERBERATORY SLAG(1) CONTAINING 11.8% ARSENIC

Size	(2) Solid/ Liquid	1 HR		24 HR		48		72		144		2304		Sample No.
		pH	%As(3)	pH	%As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4"	1:1	6.4	0.01	9.5	0.02	7.9	0.02	7.6	0.02	8.1	0.02	7.0	0.04	134-A
-8/+10 Mesh	1:1	3.8	0.02	8.8	0.02	8.9	0.03	8.7	0.03	8.1	0.04	7.2	0.05	135-A
-60/+100	1:1	9.2	0.06	9.6	0.06	9.4	0.06	8.2	0.06	7.9	0.07	8.3(4)	0.06	136-A
1/4"	1:10	6.5	0.01	7.4	0.02	7.2	0.03	6.8	0.03	7.5	0.03	5.7	0.06	134-B
-8/+10	1:10	7.2	0.002	7.9	0.04	8.1	0.04	6.9	0.04	7.1	0.04	6.2	0.08	135-B
-60/+100	1:10	8.6	0.08	9.1	0.09	8.9	0.15	8.9	0.13	9-1	0.11	7.3	0.16	136-B
1/4"	1:100	4.5	0.01	5.5	0.07	6.1	0.03	6.0	0.03	6.7	0.03	5.0	0.15	134-C
-8/+10	1:100	4.6	0.03	7.2	0.05	6.7	0.05	6.2	0.06	6.3	0.06	5.2	0.15	135-C
-60/+100	1:100	6.6	0.10	8.3	0.16	7.7	0.17	7.0	0.16	7.1	0.12	6.3	0.32	136-C

(1) Slag prepared using $FeAsO_4$ as the arsenic carrier source.

(2) Leach water starting pH was 5.7

(3) % Arsenic extracted

(4) 2040 HR.

TABLE 45. INFLUENCE OF SOLID:LIQUID RATIO AND PARTICLE SIZE ON ARSENIC EXTRACTION FROM REVERBERATORY SLAG(1) (12.0% As)

Size	Solid(2) Liquid	1 HR		24 HR		48 HR		72 HR		144 HR		2304 HR		Sample No.
		pH	%As(3)	pH	%As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4"	1:1	9.60	0.01	7.7	0.01	7.6	0.01	7.7	0.02	8.00	0.02	6.9	0.00	140-A
-8/+10 Mesh	1:1	9.50	0.03	10.0	0.06	10.1	0.05	9.3	0.05	9.8	0.05	7.3	(4) 0.03	141-A
-60/+100	1:1	9.57	0.03	9.0	0.04	9.2	0.03	8.9	0.04	8.8	0.03	7.7	(5) 0.01	142-A
1/4"	1:10	8.50	0.01	7.8	0.02	6.4	0.02	6.9	0.03	7.1	0.02	5.6	0.07	146-B
-8+10	1:10	9.08	0.03	8.8	0.04	8.3	0.05	6.7	0.05	7.2	0.07	6.5	0.02	141-B
-60/+100	1:10	9.50	0.05	9.2	0.08	9.4	0.08	7.6	0.08	8.2	0.09	6.9	(5) 0.03	142-B
1/4"	1:100	8.03	0.02	7.4	0.06	6.5	0.08	6.5	0.20	6.6	0.21	4.9	0.40	140-C
-8/+10	1:100	6.60	0.07	8.0	0.08	7.4	0.08	6.5	0.21	6.9	0.25	5.5	0.14	141-C
-60/+100	1:100	7.10	0.05	8.0	-	8.2	0.15	7.1	0.22	7.7	0.21	5.8	0.16	142-C

(1) Slag prepared using $Ca_3(AsO_4)_2$ as the arsenic carrier source
(2) Solid:Liquid Ratio
(3) Percent arsenic extracted
(4) 1680 HRS.
(5) 2040 HRS.

TABLE 46. INFLUENCE OF PARTICLE SIZE AND SOLID:LIQUID RATIO ON ARSENIC EXTRACTION FROM LEAD BLAST FURNACE SLAG(1)

(10.8% As)

Size	Solid Liquid	1 HR		24 HR		48 HR		72 HR		144 HR		2304 HR		Sample No.
		pH(3)	%As(2)	pH	%As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4	1:1	8.5	0.03	8.9	0.04	9.3	0.04	8.6	0.04	9.3	0.04	7.6	0.11	137-A
-8/+10	1:1	10.4	0.03	9.3	0.05	9.3	0.04	8.9	0.04	9.5	0.06	7.3	0.15	138-A
-60/+100	1:1	8.4	0.42	8.8	0.40	8.8	0.28	9.0	0.28	9.0	0.23	7.7	0.22	139-A
1/4	1:10	9.0	0.07	9.3	0.10	9/4	0.17	9.1	0.14	9.5	0.19	6.8	0.48	137-B
-8/+10	1:10	10.0	0.13	7.4	0.28	8.5	0.35	7.8	0.29	8.6	0.42	6.8	0.63	138-B
-60/+100	1:10	10.2	0.19	10.3	0.36	10.4	0.45	10.1	0.45	10.0	0.43	8.2	0.66	139-B
1/4	1:100	5.6	0.07	8.2	0.33	8.4	0.43	7.4	0.41	6.8	0.5	5.7	0.92	137-C
-8/+10	1:100	7.0	0.15	9.1	0.71	9.2	0.83	8.9	0.70	9.4	1.0	6.3	2.2	138-C
-60/+100	1:100	9.3	0.32	9.8	0.87	9.9	0.91	9.1	2.4	9.3	2.7	7.4	4.0	139-C

(1) $FeAsO_4$ was used as the arsenic carrier in preparing the slag.
(2) Percent arsenic extracted from the solid.
(3) The solution pH was not adjusted. It was established by the solid-liquid system.

TABLE 47. INFLUENCE OF PARTICLE SIZE AND SOLID:LIQUID RATIO ON ARSENIC EXTRACTION FROM LEAD BLAST FURNACE SLAG(1)

(13.6% As)

Size	Solid Liquid	1 HR		24 HR		48 HR		72 HR		144 HR		2040 HR		Sample No.
		pH(2)	%As(3)	pH	%As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4"	1:1	10.0	0.39	9.2	0.42	9.2	0.48	7.6	0.61	8.0	0.85	6.9	0.01	143-A
-8/+10	1:1	10.0	0.62	9.7	0.68	9.6	0.68	8.3	2.5	9.2	3.1	6.7	-	144-A
-60/+100	1:1	10.0	2.0	9.8	1.8	10.0	1.0	9.6	1.6	9.7	1.4	7.4	0.02	145-A
1/4"	1:10	9.0	0.06	8.7	0.13	8.3	0.16	7.1	0.24	7.8	0.35	6.3	0.04	143-B
-8/+10	1:10	8.8	0.12	9.4	0.21	9.4	0.21	7.7	0.33	8.4	0.59	6.5	(4) 0.107	144-B
-60/+100	1:10	9.5	0.25	10.0	0.39	10.0	0.27	9.8	0.65	9.9	0.72	7.1	0.10	145-B
1/4"	1:100	6.0	<0.01	7.6	0.02	7.8	0.05	6.8	0.14	7.1	0.21	5.6	0.21	143-C
-8/+10	1:100	6.5	0.03	8.3	0.06	8.3	0.06	7.3	0.10	7.6	0.21	6.0	0.23	144-C
-60/+100	1:100	8.0	0.05	9.0	0.10	9.3	0.13	9.5	0.18	9.7	0.24	6.6	0.56	145-C

(1) $Ca_3(AsO_4)_2$ was used as the arsenic carrier in preparing the slag.

(2) The pH was not adjusted. It was established in the solid-liquid system .

(3) Percent arsenic extracted from the solid.

(4) 2304 HR.

all tests. Particle size fractions, quoted earlier, used in the study were the same as in the slag systems. The pH range studied was 5 to 9. The results are reported in Tables 48 through 50. The test period has not been long engough to feel confident about predicted long term effect of pH.

Arsenic Content in Slags--

Most of the leach testing was performed on slag matrices that contained from 8 to 25 percent arsenic. A study was initiated to investigate the leach rates for low arsenic containing slags. Test data have only been collected for reverberatory slags. The test period was 1536 hours; therefore, trends have not, as yet, been clearly established. The results for the tests to 1536 hours are reported in Table 51.

Column Leach Tests--

Indoor--

The slags with their corresponding arsenic concentrations were leached in the column apparatus as earlier indicated and shown in Figure 6. The resulting arsenic concentrations of the leach solutions as a function of time are shown in Table 52. The high arsenic concentration can mostly be attributed to the small S/L ratios and the impaction of the leachate drops on the slag particles. This may have caused a physical breakdown in the slag. Another factor that may be important is that the slag particles were constantly in contact with the air. Should the kinetics of the arsenic dissolution be dependent upon oxygen, one can easily account for the large increase in arsenic extraction.

TABLE 48. INFLUENCE OF pH ON ARSENIC EXTRACTION FROM REVERBERATORY SLAG (11.8% As)(1)

Size	S/L(2)	1 Hour		24 Hours		48 Hours		72 Hours		144 Hours		1656 Hours		Sample #
		pH	%As(3)	pH	%As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4	1:100	5.0	0.01	5.0	0.03	5.0	0.04	5.0	0.04	5.0	0.04	5.0	0.14	134-D
-8/+10	1:100	5.0	0.03	5.0	0.07	5.0	0.10	5.0	0.08	5.0	0.08	5.0	0.24	135-D
-60/+100	1:100	5.0	0.09	5.0	0.15	5.0	0.23	5.0	0.19	5.0	0.28	5.0	0.74	136-D
1/4	1:100	7.0	0.02	7.0	0.03	7.0	0.03	7.0	0.03	7.0	0.03	7.0	0.16	134-E
-8/+10	1:100	7.0	0.03	7.0	0.08	7.0	0.08	7.0	0.08	7.0	0.08	7.0	0.16	135-E
-60/+100	1:100	7.0	0.81	7.0	0.16	7.0	0.18	7.0	0.15	7.0	0.19	7.0	0.53	136-E
1/4	1:100	9.0	0.01	9.0	0.01	9.0	0.01	9.0	0.01	9.0	0.01	9.0	0.08(4)	134-F
-8/+10	1:100	9.0	0.15	9.0	0.29	9.0	0.30	9.0	0.30	9.0	0.27	9.0	0.15(4)	135-F
-60/+100	1:100	9.0	0.08	9.0	0.17	9.0	0.24	9.0	0.29	9.0	0.25	9.0	0.55	136-F

1) Slag prepared using $FeAsO_4$ as the arsenic carrier source.
2) Solid/Liquid Ratio
3) Arsenic extracted from the solids.

TABLE 49. INFLUENCE OF pH ON ARSENIC EXTRACTION FROM REVERBERATORY SLAG (12.0% As)

Size	S/L	1 Hour		24 Hours		48 Hours		72 Hours		144 Hours		1848 Hours		Sample No.
		pH(3)	%As(2)	pH	As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4	1:100	5.0	0.02	5.0	0.06	5.0	0.06	5.0	0.20	5.0	0.27	5.0	0.27	140-D
-8/+10	1:100	5.0	0.02	5.0	0.18	5.0	0.24	5.0	0.54	5.0	0.73	5.0	0.38	141-D
-60/+100	1:100	5.0	0.10	5.0	0.35	5.0	0.49	5.0	0.52	5.0	0.70	5.0	0.61	142-D
1/4	1:100	7.0	0.01	7.0	0.02	7.0	0.04	7.0	0.09	7.0	0.09	7.0	0.12	140-E
-8/+10	1:100	7.0	0.07	7.0	0.21	7.0	0.22	7.0	0.26	7.0	0.28	7.0	0.11	141-E
-60/+100	1:100	7.0	0.06	7.0	0.46	7.0	0.51	7.0	0.45	7.0	0.49	7.0	0.15	142-E
1/4	1:100	9.0	0.01	9.0	0.02	9.0	0.04	9.0	0.04	9.0	0.05	9.0	(4) 0.07	140-F
-8/+10	1:100	9.0	0.02	9.0	0.08	9.0	0.09	9.0	0.09	9.0	0.18	9.0	(4) 0.17	141-F
-60/+100	1:100	9.0	0.07	9.0	0.21	9.0	0.23	9.0	0.26	9.0	0.32	9.0	(4) 0.20	142-F

1) $Ca_3(AsO_4)_2$ was used as the arsenic carrier in preparing the slag.
2) Percent arsenic extracted from ore solid.
3) Solution pH was not adjusted. It was established by the solid-liquid system
4) 1656 Hrs.

TABLE 50. INFLUENCE OH pH ON ARSENIC EXTRACTION FROM LEAD BLAST FURNACE SLAG(1) (13.6% As)

Size	S/L	1 Hr.										1656 Hr.		Sample No.
		(2) pH	(3) %As	pH	%As	pH	%As	pH	%As	pH	%As	pH	%As	
1/4	1:100	5.0	0.01	5.0	0.03	5.0	0.04	5.0	0.05	5.0	0.10	5.0	0.43	143-D
-8/+10	1:100	5.0	0.02	5.0	0.10	5.0	0.17	5.0	0.28	5.0	0.41	5.0	0.55	144-D
-60/+100	1:100	5.0	0.07	5.0	0.13	5.0	0.34	5.0	0.74	5.0	0.85	5.0	1.1	145-D
1/4	1:100	7.0	<0.01	7.0	0.03	7.0	0.06	7.0	0.07	7.0	0.06	7.0	0.18	143-E
-8/+10	1:100	7.0	0.02	7.0	0.07	7.0	0.25	7.0	0.25	7.0	0.35	7.0	0.22	144-E
-60/+100	1:100	7.0	0.05	7.0	0.16	7.0	0.18	7.0	0.26	7.0	0.55	7.0	0.57	145-E
1/4	1:100	9.0	<0.01	9.0	0.15	9.0	0.05	9.0	0.05	9.0	0.21	9.0	0.15(4)	143-F
-8/+10	1:100	9.0	0.03	9.0	0.04	9.0	0.15	9.0	0.13	9.0	0.15	9.0	0.21(4)	144-F
-60/+100	1:100	9.0	0.07	9.0	0.17	9.0	0.32	9.0	0.30	9.0	0.34	9.0	1.2(4)	145-F

1) $Ca_3(AsO_4)_2$ was used as the arsenic carrier in preparing the slag.
2) The pH was maintained constant
3) Percent arsenic extracted from the solid
4) 1848 Hrs.

TABLE 51. THE EXTRACTION OF ARSENIC FROM LOW ARSENIC CONTAINING REVERBERATORY SLAGS(1)

Sample #	Arsenic Source	% Arsenic in Slag	Arsenic Extracted			
			24 Hrs.		1536 Hrs.	
			%	ppm	%	ppm
11	None	0.8	0(2)	0	<0.05(3)	0.04
146	$Ca_3(AsO_4)_2$	1.1	0.03	0.03	0.09	0.10
147	$Ca_3(AsO_4)_2$	2.1	0.10	0.20	0.11	0.24
148	$Ca_3(AsO_4)_2$	3.3	0.02	0.06	0.10	0.34
149	$Ca_3(AsO_4)_2$	5.2	0	0	0.03	0.14
150	$FeAsO_4$	0.9	0	0	0.03	0.03
151	$FeAsO_4$	1.7	0	0	0.06	0.10
153	$FeAsO_4$	4.2	0	0	0.06	0.27

1) Solid:Liquid Ratio 1:100
2) Time of test was 403 hours.
3) Time of test was 8304 hours.

TABLE 52. ARSENIC CONCENTRATION IN COLUMN LEACHWATERS

	Calcium arsenate in copper reverberatory slag		
	Sample No. 1	Sample No. 2	Sample No. 2
Size	1/4 in.	1/2 in.	1/4 in.
Slag, As %	15.7	15.7	5.0
S/L ratios	1:1	1:1	1:10
Time, hrs.	Arsenic extraction (ppm)		
24	16.7	0.05	0.84
48	19.5	10.0	2.4
72	18.3	14.7	4.3
144	18.6	15.2	5.0
3,672	-	-	7.2
4,464	-	27.6	-
4,512	31.2	-	-

In the column leaches oxygen is readily available while in the shake leach or similar tests the available amount of oxygen is dependent upon the dissolved oxygen content of the leach solution.

It should also be noted that arsenic extraction increases as the particle size decreases. In a likewise manner, arsenic extraction also increases as the original arsenic concentration of the slag increases.

Outdoor--

Seven slag samples were exposed to the action of precipitation in the environment. The arsenic concentration in the leach solution as a function of time are shown in Table 53. Different trends can be seen when these arsenic data are further analyzed. Using the copper reverberatory slag as the retaining matrix, it appeared that arsenic was precipitating from the leach solution after 3000 hours. This would account for the decrease in arsenic concentration with the increase in time. Using the lead blast furnace slag, just the opposite trends were noted. If the iron arsenate was used as the arsenic form to be dissolved in the slag, the arsenic concentration of the leachate increased with time. If calcium arsenate was used, the arsenic concentration seemed independent of time and remained fairly constant at 0.90 ppm As.

Clays

Many studies have been reported on the adsorption and absorption of arsenic by clays, especially the kaolinite and

TABLE 53. ARSENIC CONCENTRATION IN OUTDOOR SLAG LEACH WATERS

Sample No.	Sample Description	Slag As%	Time Hrs.	As Extr. ppm	Time Hr.	As ppm	Time Hr.	As ppm	Time Hr.	As ppm
1	Copper Rev. Slag	0.54	2952	0.02	4632	0.02	6144	0.05	7320	0.07
2	Lead B. F. Slag	0.27	2952	0.03	4632	0.02	6144	0.07	7320	0.07
3	Iron arsenate + L.B.F. Slag	10.2	2952	0.90	4632	0.85	6144	01.9	7320	1.4
4	Iron arsenate + C.R. Slag	8.9	2952	0.84	4632	0.70	6144	0.64	7320	0.27
5	Calcium arsenate + C.R. Slag	12.9	2952	0.53	4632	0.36	6144	0.48	7320	0.40
6	Calcium arsenate +L.B.F. Slag	15.6	2952	0.92	4632	0.89	6144	0.85	7320	0.90
7	Blank (no slag)	-	2952	< 0.02	4632	< 0.02	6144	<.02	7320	<0.02

L.B.F. = Lead blast furnace.
C.R. = Copper reverberatory.

montmorillonite type clays. These studies and more have been surveyed before, Mehta, 1981 (6). A major objective of reacting clays with the arsenic compounds was to produce a stable compound that could be disposed of in a landfill site. Although such a site would still require a liner in order to prevent migration of arsenic to the ground water, attenuation studies have been reported where clay liners were used, Korte, et. al., 1976 (7) and Griffin, 1976 (8). The present approach was to physically impound the slightly soluble arsenates such as calcium or iron arsenates in a clay matrix.

The arsenate-clay mixture was formed into small pellets, then roasted to give dense and physically strong pellets which could be buried for storage. Initially, such pellets were re-coated with clay and roasted again to form a barrier, but it broke off easily upon handling. A low-temperature melting ceramic glaze was used as a barrier. The pellets were formed by using a hydraulic press at two ton per square inch pressure.

The pellets were leached to determine arsenic extraction by shake test. The extractions as functions of time are shown in Table 54. Both iron and calcium arsenate pellets made with varying amounts of bentonite clay showed low arsenic extraction upon leaching even when no glaze was applied. Glazing does not seem to significantly result in lower extractions. Slag matrix releases arsenic more rapidly than a clay matrix. Fly ash from a lime scrubbing unit of a power plant has a lot of calcium to provide an alkali matrix. Such a matrix appears to work well

TABLE 54. PELLET DATA

No.		hr	As(ppm)	hr	As(ppm)	hr	As(ppm)
1	75% $FeAsO_4$ + 25% Bentonite	1	0	96	0.08	9120	0.26
2	50% $FeAsO_4$ + 50% Bentonite	1	0	96	0.30	9120	0.19
3	25% $FeAsO_4$ + 75% Bentonite	1	0	96	0	9120	0.15
4	90% $FeAsO_4$ + 10% Glaze	1	0	96	0.07	9120	0.15
5	80% $FeAsO_4$ + 20% Glaze	1	0	72	0.11	9096	0.68
6	50% $FeAsO_4$ + 40% Bentonite + 10% Glaze	1	0.02	72	0.02	9096	0.11
7	30% $FeAsO_4$ + 60% Bentonite + 10% Glaze	1	0.03	72	0.01	9096	0.11
8	65% $FeAsO_4$ + 25% L.B. Furnace Slag + 10% Glaze	1	0.02	96	0.14	9120	2.28
9	40% $FeAsO_4$ + 50% L.B. Furnace Slag + 10% Glaze	1	0.03	72	0.24	9096	1.87
10	75% $FeAsO_4$ + 25% L.B. Furnace Slags	1	0.52	72	23.8	9096	78
11	25% $FeAsO_4$ + 75% L.B. Furnace Slags	1	0.03	96	0.08	9120	0.75
12	50% $FeAsO_4$ + 50% Fly Ash	1	0.07	96	0	9120	0.22
13	50% $FeAsO_4$ + 40% Fly Ash + 10% Glaze	1	0.04	96	0.15	9120	1.12
14	75% $Ca_3(AsO_4)_2$ + 25% Bentonite	1	0.08	96	0.05	9120	0.04
15	50% $Ca_3(AsO_4)_2$ + 50% Bentonite	1	0.02	96	0.03	9120	0.04
16	25% $Ca_3(AsO_4)_2$ + 75% Bentonite	1	0.05	96	0.01	9120	0.04
17	90% $Ca_3(AsO_4)_2$ + 10% Glaze	1	0	96	0	9120	5.73
18	80% $Ca_3(AsO_4)_2$ + 20% Glaze	1	0	96	0	9120	3.12
19	50% $Ca_3(AsO_4)_2$ + 40% Fly Ash + 10% Glaze	1	0	96	0	9120	0.04
20	40% $Ca_3(AsO_4)_2$ + 50% Bentonite + 10% Glaze	1	0	96	0.01	9120	0.04

with another caustic material such as calcium arsenate than a non-caustic material such as iron arsenate.

Previous studies, mentioned earlier, have stated that the principal adsorption mechanism for arsenic is anion exchange. Valency of the metal is also a significant factor. Thus, As (V) is more readily absorbed than As (III). Esson, et. al., 1965 (9) have argued that, in the clays, arsenic is probably accepted into octahedral sites usually occupied by Fe (III), Mg (II), Ti (IV), and Al (III), and that there is some arsenic substitution for Si (IV) and Al (III). But the clays, aluminosilicates, do not show high concentrations of arsenic because arsenic probably was not available in its higher oxidation state although, in this state, arsenic is similar chemically to Fe (III), Al (III), and Si (IV).

Previous attenuation studies reported reacting a specific amount of arsenic, either As (III) or As (V), in a specific amount of leaching medium with a specific amount of clay to note the decrease in the equilibrium arsenic concentration in the leachate. In an attempt to arrive at the same situation, but from the opposite direction, a specific amount of clays was reacted with a specific amount of both As (III) and As (V). This was done by pelletizing the mixture, drying, and roasting the pellets at various temperatures. Roasting was supposed to aid the adsorption mechanism and also bring arsenic to the higher oxidation state when occurring as As (III). After roasting, the pellets were weighed and leached at 1:100 S/L ratio for various intervals of time. These data are shown in Tables 55 through 62. T 55-62

TABLE 55. REACTION OF As_2O_3 WITH BENTONITE (0.25% As)

No.	% As Ideal	% As Assayed	Treatment		Arsenic Extraction (ppm)		
			Temp °C	Time Min.	1 hr.	24 hrs.	168 hrs.
1	0.25	0.29	100	15	7.2	8.0	26
2		0.30		30	5.4	11.0	21
3		0.30		45	4.7	5.1	16
4		0.30		60	1.8	18	30
5	0.25	0.30	200	15	13	34	23
6		0.27		30	12	14	30
7		0.27		45	4.3	5.4	14
8		0.26		60	6.8	8.1	18
9	0.25	0.26	300	15	4.4	9.1	19
10		0.26		30	6.6	14	20
11		0.25		45	5.1	20	20
12		0.25		60	8.4	14	18
13	0.25	0.27	400	15	4.8	10	21
14		0.27		30	8.4	20	21
15		0.26		45	11	18	34
16		0.26		60	4.8	18	22
17	0.25	0.26	--	--	6.8	9.1	12

TABLE 56. REACTION OF As_2O_3 WITH BENTONITE (0.50% As)

No.	% As Ideal	% As Assayed	Treatment		Arsenic Extraction (ppm)		
			Temp °C	Time Min.	1 hr.	24 hr.	168 hrs.
18	0.50	0.53	100	15	5.7	7.0	25
19		0.53		30	7.7	22	31
20		0.53		45	4.0	6.0	19
21		0.62		60	6.6	11	18
22	0.50	0.55	200	15	6.5	12	30
23		0.54		30	9.0	20	30
24		0.54		45	11.	17	47
25		0.52		60	7	12	25
26	0.50	0.56	300	15	2.5	18	27
27		0.51		30	7.7	20	30
28		0.74		45	7.2	12	31
29		0.87		60	7.9	23	33
30	0.50	0.53	400	15	3.2	22	43
31		0.50		30	3.4	8.2	22
32		0.51		45	6.3	40	45
33		0.50		60	7.8	27	37
34	0.50	0.49			5.0	8.0	17

TABLE 57. REACTION OF As_2O_3 WITH BENTONITE
(0.75% As)

No.	% As Ideal	% As Assayed	Pretreatment Temp ^oC	Pretreatment Time Min.	Arsenic Extraction (ppm) 1 hr.	24 hr.	168 hrs.
35	0.75	0.77	100	15	23	25	68
36		0.81		30	34	38	45
37		0.85		45	18	39	54
38		0.85		60	20	62	66
39	0.75	0.85	200	15	24	42	52
40		0.80		30	7.9	20	20
41		0.83		45	-	-	-
42		0.83		60	1.2	3.0	10
43	0.75	0.80	300	15	71	95	69
44		0.80		30	23	24	39
45		0.83		45	7.4	29	50
46		0.83		60	15	49	61
47	0.75	0.83	400	15	15	53	61
48		0.80		30	14	34	72
49		0.80		45	15	17	39
50		0.79		60	13	31	48
51	0.75	0.84	-	-	29	34	52

TABLE 58. REACTION OF As_2O_3 WITH BENTONITE (1.0% As)

No.	% As Ideal	% As Assayed	Temp °C	Pretreatment		Arsenic Extraction (ppm)	
				Time Min.	1 hr.	24 hr.	168 hrs.
52	1.0	0.78	100	15	18	26	42
53		0.53		30	7.8	17	25
54		0.74		45	11	30	52
55		0.76		60	10	18	44
56	1.0	0.78	200	15	34	60	83
57		0.82		30	17	39	49
58		0.82		45	13	34	48
59		0.80		60	5.3	20	30
60	1.0	0.80	300	15	13	17	52
61		0.68		30	35	54	56
62		0.48		45	43	66	58
63		0.50		60	19	32	42
64	1.0	0.50	400	15	35	62	58
65		0.72		30	26	57	63
66		0.72		45	43	55	59
67		0.72		60	23	38	65
68	1.0	0.76	-	-	29	52	66

TABLE 59. REACTION OF As_2O_5 WITH BENTONITE
(0.25% As)

No.	% As Ideal	% As Assayed	Pretreatment Temp °C	Pretreatment Time Min.	Arsenic Extraction (ppm) 1 hr.	Arsenic Extraction (ppm) 24 hr.	Arsenic Extraction (ppm) 168 hrs.
69	0.25	0.29	100	15	49	92	88
70		0.26		30	39	61	80
71		0.30		45	37	78	87
72		0.25		60	12	15	15
73	0.25	0.27	200	15	5.5	10	19
74		0.26		30	10	18	32
75		0.26		45	8.0	18	32
76		0.26		60	6.2	12	19
77	0.25	0.27	300	15	11	14	17
78		0.27		30	15	20	20
79		0.26		45	22	27	19
80		0.28		60	8.0	24	17
81	0.25	0.29	400	15	22	26	24
82		0.25		30	24	28	53
83		0.23		45	15	27	24
84		0.27		60	6.1	22	18
85	0.25	0.26	-	-	6.8	27	22

TABLE 60. REACTION OF As_2O_5 WITH BENTONITE (0.5% As)

No.	% As Ideal	% As Assayed	Pretreatment		Arsenic Extraction (ppm)		
			Temp °C	Time Min.	1 hr.	24 hr.	168 hrs.
86	0.50	0.47	100	15	19	34	35
87		0.48		30	25	34	50
88		0.52		45	20	47	46
89		0.49		60	4.1	12	35
90	0.50	0.50	200	15	30	42	52
91		0.47		30	6.7	27	36
92		0.46		45	17	33	40
93		0.47		60	37	60	45
94	0.50	0.49	300	15	5.7	16	37
95		0.44		30	37	57	44
96		0.47		45	36	49	46
97		0.45		60	33	30	48
98	0.50	0.44	400	15	23	32	43
99		0.59		30	5.4	15	30
100		0.44		45	42	59	49
101		0.43		60	19	17	48
102	0.50	0.49	-	-	29	31	41

TABLE 61. REACTION OF As_2O_5 WITH BENTONITE (0.75% As)

No.	% As Ideal	% As Assayed	Pretreatment		Arsenic Extraction (ppm)		
			Temp °C	Time Min.	1 hr.	24 hr.	168 hrs.
103	0.75	0.85	100	15	55	100	87
104		0.77		30	61	66	83
105		0.88		45	42	102	81
106		0.92		60	36	68	83
107	0.75	0.88	200	15	25	51	78
108		1.16		30	34	56	63
109		0.88		45	4.8	35	109
110		0.88		60	65	96	81
111	0.75	0.75	300	15	78	107	96
112		0.87		30	22	47	66
113		0.93		45	79	83	60
114		1.20		60	28	35	51
115	0.75	0.72	400	15	27	29	69
116		0.65		30	68	64	63
117		0.58		45	1.2	23	66
118		0.89		60	49	44	66
119	0.75	0.84	-	-	68	98	88

TABLE 62. REACTION OF As_2O_5 WITH BENTONITE (1.0% As)

No.	% As Ideal	% As Assayed	Treatment		Arsenic Extraction (ppm)		
			Temp °C	Time Min.	1 hr.	24 hr.	168 hrs.
120	1.0	0.91	100	15	65	109	89
121		0.90		30	49	128	98
122		0.90		45	83	122	85
123		0.88		60	82	123	100
124	1.0	0.88	200	15	61	114	90
125		0.90		30	80	107	91
126		1.02		45	39	103	78
127		.94		60	13	34	57
128	1.0	0.96	300	15	51	81	86
129		0.86		30	78	98	82
130		0.86		45	64	65	77
131		1.06		60	114	108	88
132	1.0	0.90	400	15	69	105	100
133		0.92		30	4.8	23	63
134		0.84		45	105	95	82
135		0.94		60	2.6	10	74

Arsenic trioxide has a solubility of 3.7 gm/100 ml at 20°C and arsenic pentoxide has a solubility of 150 gm/100 ml at 16°C. In Table 55, pellet numbered 18 has arsenic extraction after 168 hours at 25 ppm. In Table 59, pellet numbered 86 has arsenic extraction after 168 hours at 35 ppm. In Table 59, pellet numbered 94 has arsenic extraction of 37 ppm after 168 hours. Arsenic contents in both cases were about 0.5 percent or 5300 μg per gm in the first case and 4900 μg per gm in the second case. These amounts were leached with 100 ml of water at room temperature. Considering the solubilities for both arsenic trioxide and arsenic pentoxide, the arsenic contents in these two pellets, and the other pellets as well, should have dissolved completely if not after one hour then after 168 hours. Although the arsenic extraction increases as the time interval increases, still the extracted arsenic is nowhere close to its solubilities in (III) and (V) states. The extraction as a function of time should be of some interest to us if continued for a longer period of time to determine arsenic extraction.

If the clay leaching characteristics are predetermined, multi-layer clay beds could be used to ward off any arsenic going into the ground water. It is apparent from these data, that arsenic is reluctantly released by the clays even when the worst-case leaching is applied to them.

Cements and Concretes

Cements--

Arsenic trioxide and calcium arsenate have been used in portland cement mixtures for special uses. Introduction of arsenic in cement has been reported to have resulted in retardation in early-setting time, increase in early high strength. Its presence in cements has also been reported to have produced resistance to the chemical action of water in those cements, Mehta, 1977 (3). Addition of arsenic compounds to cements has been restricted to low quantities as arsenic in increased amounts produces retardation in cement setting.

Experiments were carried out to mix various amounts of arsenic compounds with cement and notice the resulting cement blocks for setting. Samples containing about 25 percent or less of the arsenic compounds showed sound structures although no effort was made to characterize any of the physical properties. Samples containing a high percentage of arsenic compounds definitely failed to form a good castable cement. Since the major reason for the setting of cements into hard and dense structures is the crystallization of tricalcium silicate ($3CaO \cdot SiO_2$), any retardation in its formation did not produce a solid sample. Retardation at higher arsenic percentages was so enhanced that the final product was soft and crumbly.

Leaching characteristics of some of the samples made with varying amounts of arsenic compounds are presented in Table 63.

TABLE 63. CEMENT DATA

No.	Composition	%As	Arsenic Extraction ppm				
			1 hr.	24 hrs.	48 hrs.	192 hrs.	9288 hrs.
1	10%As_2O_3		0.41	1.0	1.7	4.1	2.3
2	25%As_2O_3		1.8	10.3	16.1	27.0	24.0
3	50%As_2O_3		22	102	152	470	580
4	10%FA		0.04	0.24	0.38	0.39	0.52
5	25%FA		0.12	0.47	0.62	0.64	0.85
6	50%FA		2.1	9.4	13.8	3.12	3.8
7	50%CA		0.19	0.80	1.5	0.34	0.06

No prior treatment was given to the samples. The mixtures were wetted and cast in one inch cube.

FA = Ferric arsenate.
CA = Calcium arsenate.

Arsenic extraction of the samples is reported as a function of time. The samples were prepared with cement and various arsenic compound, cast in plastic trays to give approximately one inch cubes, and cured in water for seven days. After washing and drying, the samples were subjected to the shake leach test described earlier.

Arsenic trioxide samples with cement show continuous extraction of arsenic in excessive amounts. Arsenic extraction is a function of both time of leaching and the initial arsenic present. At higher arsenic amount, the cement cube was soft and it crumbled easily. This exposes more surface area for arsenic to leach out.

Iron arsenate shows lower arsenic solubilities but, as can be seen from Table 62, the initial concentration of arsenic is lower to start with. Also, the comparatively lower solubility of iron arsenate to that of arsenic trioxide would be a factor in small amounts of arsenic extracted. A point of interest is that arsenic extraction reaches a peak, then starts decreasing. This has been observed not only here but elsewhere, too. One possible explanation may be that arsenic may have precipitated out of the solution again as insoluble arsenite or arsenate at the high pH values of the cement leach systems.

Again, high arsenate and cement mixtures were soft and crumbly. In the case of calcium arsenate, results for only

50-50 percent mixtures are available. Although the cement sample disintegrated upon shake leaching, arsenic extraction was lowest of these systems. This is probably due to the fact that excessive amounts of calcium are present not only in the cement, but also in calcium arsenate to react with any arsenic going into solution.

The relationship between the curing time and the arsenic extraction upon leaching of the cement is given in Table 64. The previous experiments showed that the high arsenic trioxide contents in the cements did not produce a sound sample. The highest arsenic content was limited to 25 percent arsenic trioxide or about 18 percent arsenic. The samples were cured for seven days, fourteen days, or thirty days.

The data indicate that the curing period has no distinct relationship with the arsenic release. The extraction depends clearly upon the quantity of arsenic present originally. Although the arsenic extraction increases with time during the initial leaching stages, it reverses its trend after some time. It would be impractical if not impossible to monitor the point at which the reversal takes place. This reversal is the only significant matter of interest.

Another effort was made to determine if prior heating of the cement samples could have any effect on arsenic extraction upon leaching. A few samples experimented with this approach are presented in Tables 65 and 66. The heating or roasting took place at three different temperatures. The roasting period was kept

TABLE 64. INFLUENCE OF CURING TIME ON ARSENIC EXTRACTION FROM CEMENT SAMPLES

	7 Day Cure Arsenic Extraction (ppm)					14 Day Cure Arsenic Extraction (ppm)					30 Day Cure Arsenic Extraction (ppm)				
%As_2O_3	24 hr.	48 hr.	72 hr.	144 hr.	6360 hr.	24 hr	48 hr.	72 hr.	144 hr.	6192	24 hr.	48 hr.	72 hr.	144 hr.	5832 hr.
2%		0.12		1.14	0.15	0.37	0.48	0.12	1.4	0.15	0.17	0.12	0.27	0.43	0.05
4%		0.096		0.95	0.60	0.45	0.48	0.36	0.76	0.34	1.07	0.83	0.83	0.93	0.48
6%		0.42		0.36	0.60	1.43	1.31	1.43	0.43	0.56	2.02	1.16	0.62	0.98	0.15
8%		0.48		1.21	4.50	2.65	1.4	2.14	1.66	1.12	2.73	1.79	1.79	1.91	0.79
10%		0.77		3.45	4.57	3.21	2.38	2.17	0.95	1.72	1.07	1.9	1.41	2.02	0.98
15%		9.05		9.5	6.09	10	12.14	7.86	8.81	7.14	6.31	2.19	9.17	8.52	6.96
20%		15		14.76	7.52	11.9	3.09	5.77	11.67	7.52	29.76	2.38	15		8.28
25%		13.81		14.29	7.52	14.76	13.33	15.7	15.71	7.33	11.43		35.7		7.43

TABLE 65. INFLUENCE OF ROAST TREATMENT ON ARSENIC EXTRACTION FROM CEMENT SAMPLES

			Roast Treatment		Arsenic Extracted in ppm				
No.	Composition	%As	Temp. °C	Time Hr.	1 hr.	24 hr.	48 hr.	192 hrs	9072 hrs.
1	10% CA	4.1	200	1	0.07	0.22	0.35	0.75	0.74
2	10% CA	4.1	400	1	0.06	0.09	0.10	0.04	0.02
3	10% CA	4.1	600	1	0.07	0.04	0.07	0.04	0.02
4	25% CA	10.3	200	1	0.38	1.36	1.44	1.1	1.0
5	25% CA	10.3	400	1	0.18	0.98	0.88	0.19	0.30
6	25% CA	10.3	600	1	0.02	0.03	0.10	0.04	0.02
7	50% CA	20.6	200	1	3.3	12.1	17.0	1.4	1.6
8	50% CA	20.6	400	1	2.7	9.4	12.0	2.6	1.7
9	50% CA	20.6	600	1	0.13	0.31	0.38	0.04	0.07
10	10% FA	2.5	200	1	0.06	0.21	0.29	0.08	0.30
11	10% FA	2.5	400	1	0.02	0.06	0.06	0.04	0.20
12	10% FA	2.5	600	1	0.02	0.02	0.03	0.04	0.13
13	25% FA	6.3	200	1	0.09	0.37	0.50	1.1	2.0
14	25% FA	6.3	400	1	0.09	0.47	0.74	0.69	2.2
15	25% FA	6.3	600	1	0.09	0.32	0.41	0.19	0.09
16	50% FA	12.5	200	1	0.56	3.3	4.3	7.1	6.6
17	50% FA	12.5	400	1	0.76	3.2	3.8	1.8	3.5
18	50% FA	12.5	600	1	0.29	1.3	1.7	3.1	4.4

The arsenate and cement mixture was roasted, then wetted and cast in one inch cube.

CA=Calcium Arsenate
FA=Iron Arsenate

TABLE 66. INFLUENCE OF ROAST TREATMENT ON ARSENIC EXTRACTION FROM CEMENT SAMPLES

No.	Composition	%As	Roast Treatment		Arsenic Extracted ppm				
			Temp^{o}C	Time Hr.	1 hr.	24 hr.	48 hrs.	192 hrs.	9288hrs.
1	10%CA	3.2	200	1	0.18	1.4	1.8	0.15	0.04
2	10%CA	3.2	400	1	0.19	0.47	0.62	0.41	0.04
3	10%CA	3.2	600	1	0.06	0.29	0.38	0.02	0.02
4	25%FA	6.0	200	1	0.06	0.29	0.41	1.17	1.0
5	25%FA	6.0	400	1	0.15	0.41	0.50	0.14	0.74
6	50%FA	14.2	200	1	0.41	1.28	1.57	–	4.0

One inch cement cube which was roasted after casting and curing.

one hour. Although this may seem to be arbitrary, preliminary experiments had shown this time period to be of sufficient duration. Removal of any volatile arsenic and increased reaction of the arsenic compounds with cement were the chief objectives of such a roasting treatment.

Three cement samples with ten percent calcium arsenate were roasted at 200°, 400°, and 600°C. Roasting at higher temperatures resulted in lower arsenic extraction. These data are shown in Table 65. The same procedure was used for iron arsenate. It, too, showed the same trend which is not discussed here because of lack of sufficiently comparable data points. These experiments were performed on previously cast cement cubes. As a variation to this roasting treatment of the cement samples, cement and calcium and iron arsenates in different proportions were roasted before wetting and casting. The results are presented in Table 66. Again, roasting at higher temperatures resulted in lower arsenic extractions. Although the cement samples with high arsenic compounds did not produce hard and sound structures - even very crumbly at 50-50 mixtures - arsenic release is low. The alkalinity of the leach systems with abundant calcium ion supply would have reacted with any soluble arsenic to cause its precipitation out of the leach system.

Concrete--

Attempts at casting concrete samples containing cements with arsenic compounds resulted in poor concrete structures. Arsenic concentrations were required at very low levels to produce a good structure. These difficulties prompted the idea of using the arsenical slag as a filling material for concrete mixes. Preliminary work at casting such concretes mixes proved very successful and resulted in sound structures. It will be noted though no physical testing was done on these samples. Factors such as curing periods and sizes of the slag were found to have no significant effect on arsenic extraction. All the samples were leached at 1:100 solid to liquid ratios. It is assumed that different S/L ratios would have an effect on the arsenic extraction. No work involving various S/L ratios was attempted because of the multiplicity of the samples involved in such work. The data on concrete work are presented in Tables 67 and 68.

The data presented on leaching characteristics of cements and concretes should be judged on the basis of a sound monolithic structure. What happens if the structure were to break down and expose more surface area for arsenic to leach out is hard to predict. Total immersion tests, as applied here, require a careful interpretation of the leach data. One useful way to do so would be to take into account the mass of arsenic leached to that of total arsenic initially present in the sample. This type of interpretation is certainly helpful when considering different configurations and sample volumes, Colombo and Neilson, 1977 (10).

TABLE 67. SLAG-CONCRETE DATA

No.	% As in Concrete Slag mix	Size of Slag	Curing Days	Arsenic Extraction (ppm)				
				24 hrs.	48 hrs.	144 hrs.	hr.	As ppm
1	2.3	½ inch	7	< 0.02	0.02	0.05	5880	< 0.02
2	4.2	½ inch	7	< 0.02	< 0.02	0.02	6216	0.02
3	2.6	½ inch	15	< 0.02	0.14	0.21	6384	< 0.02
4	3.2	½ inch	15	< 0.02	0.31	0.36	6384	0.02
5	2.6	½ inch	30	< 0.02	0.02	0.07	6384	0.02
6	4.2	½ inch	30	< 0.02	0.03	< 0.02	6384	< 0.02
7	3.4	-80 mesh	7	< 0.02	0.07	0.14	—	—
8	4.2	-80 mesh	7	< 0.02	0.05	0.24	5880	< 0.02
9	4.2	-80 mesh	15	< 0.02	0.02	0.19	5880	0.03
10	3.4	-80 mesh	30	< 0.02	0.02	0.02	5544	< 0.02
11	4.2	-80 mesh	30	< 0.02	0.03	0.02	5208	< 0.02

Nos. 1, 3, 5, 7, and 10 had 20% of the mixture as slag

Nos. 2, 4, 6, 8, 9, and 11 had 25% of the mixture as slag.

The concrete mixes had the following compositions:

200 gm gravel	187.5 gm gravel
200 gm cement	187.5 gm cement
400 gm sand	275.0 gm sand
200 gm slag, or	250.0 gm slag

TABLE 68. SLAG-CONCRETE DATA

No.	% As in Concrete Slag Mix	Size of Slag	Arsenic Extraction (ppm)				
			1 hr.	24 hr.	48 hrs.	72 hrs.	144 hrs.
1	1	¼ inch	0.06	0.07	0.04	0.04	< 0.02
2	2	¼ inch	0.04	0.04	0.04	0.07	< 0.02
3	3	¼ inch	0.06	0.04	0.07	0.04	< 0.02
4	5	¼ inch	0.02	0.04	0.04	0.04	< 0.02
5	10	¼ inch	0.02	0.11	0.04	0.04	< 0.02
6	1	-8/+10 mesh	0.02	0.04	0.04	0.04	< 0.02
7	2	-8/+10 mesh	0.02	0.07	0.04	0.07	< 0.02
8	3	-8/+10 mesh	0.02	0.04	0.07	0.04	< 0.02
9	5	-8/+10 mesh	<0.02	0.04	0.04	0.04	< 0.02
10	1	-60/+100 mesh	0.02	0.04	0.04	0.04	< 0.02
11	2	-60/+100 mesh	0.02	0.04	0.04	0.04	< 0.02

Concrete mixes contained 20% slag by weight.
They were made of the following composition:

200 gm gravel
200 gm cement
400 gm sand
200 gm slag

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APPENDIX A

FIXATION OF ARSENIC BY LIME ROASTING

SYMBOLS AND TERMS

Arsenic:	The terms arsenic and arsenic trioxide (As_2O_3) are used synonymously throughout this thesis as it is a standard practice in the industry.
Retention:	Retention means arsenic left behind either in the reacted form, unreacted form, or unvolatilized form.
Getter:	A term applied to a substance that would prevent arsenic from volatilizing at high temperatures by a chemical reaction between the getter and arsenic to form a non-volatile compound.
w/o:	Weight %.

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SECTION 1

INTRODUCTION

In smelting operations, due to the finely divided nature of the feed material, dust is created which is called "flue dust". This flue dust is carried by the moving gases from the roasters and furnaces. A part of the dust is settled and recovered in the flue system by flue chambers; the bulk of it is captured by electrostatic precipitators or in baghouses.

As mentioned earlier, the flue dust contains valuable metals and thus it is not economical to throw the material away (Table 1). At the same time, it contains arsenic which would leach out and enter the hydrosphere at detrimental levels. Open dumping in this case is not advisable.

BACKGROUND

In any high temperature operation such as roasting and smelting, evolution of fine dust takes place which is entrained by the moving gases and carried away into the flue system. Most of the particulate matter in flue dust is collected in the flue system by using flue chambers, cyclones, and electrostatic precipitators. Since the high strength SO_2 off-gas is controlled by an acid plant, the gas stream is further cleaned of its particulate

TABLE 1. COMPOSITION OF THE FLUE DUST

Element	%	*oz/t
Arsenic	17.5	
Copper	8.2	
Zinc	5.9	
Lead	4.1	
Iron	12.7	
Cadmium	0.30	
Antimony	0.35	
Bismuth	0.38	
Tin	0.48	
Sulfur (total)	9.3	
Silver*	7.4*	

matter by using baghouses. Particulate matter gathered along the collection points in the flue system is received in the hoppers. These are the dust origin points. By controlling the velocity, volume, and the temperature of the moving gas stream, volatile constituents such as As_2O_3 may be made to deposit along with the particulate matter.

SCOPE AND OBJECTIVE

The primary objective of this investigation was to study compounds that would act not only as arsenic-getters but also as stabilizers by converting the principal form of arsenic (As_2O_3) occurring in the flue dust to a more stable form such as an arsenate.

It was desired that the arsenic retention and the chemical conversion take place by a simple process of pelletizing these compounds with arsenic and roasting the pellets at low temperatures to effect the chemical conversion.

The following were studied under the stated objective:

1. Arsenic retentions at different arsenic to arsenic-getter compound weight ratios
2. Arsenic retentions at different temperatures for different intervals of time

These two were determined by chemical analysis of the resulting products.

3. Chemical conversion of arsenic in the final product

This was determined by x-ray diffraction traces of the product.

SECTION 2

CONCLUSIONS

Calcium compounds have been found to perform best as arsenic-getters. Arsenic combines with calcium to form calcium arsenate, $Ca_3(AsO_4)_2$. Better than 97 percent of the arsenic is retained in the product when the pellets of arsenic and calcium compounds, especially CaO and $Ca(OH)_2$, are roasted at low temperatures using the stoichiometric compositions. Arsenate formation was rapid (within 30 minutes) even at low experimental temperatures (200° to 400°C).

In order to form calcium arsenate, the calcium content needs to occur as either lime, hydrated lime, or limerock. Other calcium forms are not as effective as these three in retaining arsenic.

Iron and aluminum compounds do not show high arsenic retentions. These substances are not reactive with arsenic to form iron arsenate or aluminum arsenate. Arsenic is lost by volatilization at the roasting temperatures.

X-ray diffraction analysis has confirmed the conversion of arsenic to arsenate form using the lime group. The presence of arsenates was not confirmed using the other getters from the iron group and the aluminum group.

SECTION 3

RECOMMENDATIONS

Calcium arsenate formation using As_2O_3 and lime as the getter at low temperatures is shown to be successful. Further work is not necessary, in this case, either reacting the materials in the dry state or the wet state. Use of the pelletization and low temperature roast is recommended as opposed to the precipitation of calcium arsenate from the aqueous media. This will do away with the steps of arsenic dissolution, reaction, thickening, filtering, and drying which are required in the aqueous precipitation of calcium arsenate.

Although this product has high water solubility characteristics, it can be contained by dissolution in a molten slag.

Iron arsenate has the lowest water solubility characteristics of all the arsenates followed by aluminum arsenate. In a porous pellet such as a hand-formed pellet, the retention time for arsenic to react with either iron or aluminum compounds is very short. This retention time can be increased by mechanical press forming of the pellet whereby a dense structure is obtained. Here again, even if the process is successful in forming the arsenates upon roasting, the product may still have problems regarding open disposal practices. In this case, too, the products can be disposed of in a smelter molten slag.

SECTION 4

MATERIALS AND METHODS

FLUE DUST ORIGIN

This dust was obtained from a copper smelter in the Western United States. The dust originated in the baghouse at the smelter. Although the point of collection of the dust is known, no specific source is mentioned as the dust may have been a result of the materials handling, roasting, smelting, or converting.

Chemical Analysis of the Flue Dust

A chemical analysis of the flue dust sample is given with regard to the major elements of interest:

As%	Cu%	Zn%	Pb%	Fe%	Cd%	Sb%
17.7	8.2	5.9	4.1	12.7	0.30	0.35

Form of Arsenic in the Flue Dust

An X-ray diffraction trace was obtained of the sample. The form of arsenic is shown to be As_2O_3. It is believed that a part of this arsenic is tied up as arsenates of various metals. In high temperature operations, some of the arsenic As(III) is oxidized to As(V) forming As_2O_5 which reacts with other metals to form arsenates. Although it was hard to confirm their presence by X-ray diffraction work, a previous work has shown such arsenates to be present in similar dusts, Knopke, 1974 (1).

SELECTION OF THE ARSENIC-GETTER COMPOUNDS

Arsenic in the flue dust is predominantly in the form of As_2O_3. This compound is more soluble in water as compared to the other compounds of arsenic. Water percolating through a landfill site containing such arsenic waste may show high concentrations of arsenic in the ground water or run-off water. If arsenic could be converted to the arsenate form, which has lower solubility characteristic, its disposal could be maintained in a chemical pond, Mohri and Yamada, 1976 (2). Furthermore, if chemical ponding was not desirable because of maintenance problems, the arsenate could be dissolved in smelter slag, Mehta, 1980 (3).

The selection of the getters was based, therefore, upon a study of the arsenates. The range of metal arsenates from calcium arsenate to iron arsenate exhibit lower solubilities of arsenic in aqueous medium than does As_2O_3. These solubilities are shown in Table 2.

TABLE 2. AQUEOUS SOLUBILITY OF METAL ARSENATES, CHUKHLANTSEV, 1956 (4)

Compound	Solubility product constant, K_{sp}	AsO_4^{3-} concentration (moles/liter)
$Ca_3(AsO_4)_2$	6.8×10^{-19}	1.8×10^{-4}
$Mg_3(AsO_4)_2$	2.1×10^{-20}	9.1×10^{-5}
$Zn_3(AsO_4)_2$	1.3×10^{-28}	2.1×10^{-6}
$Cd_3(AsO_4)_2$	2.2×10^{-33}	2.3×10^{-7}
$Pb_3(AsO_4)_2$	4.1×10^{-36}	6.6×10^{-8}
$AlAsO_4$	1.6×10^{-16}	1.2×10^{-8}
$FeAsO_4$	5.7×10^{-21}	7.6×10^{-11}

Previous works, as discussed in the literature survey of Arsenic Metallurgy, Mehta, 1980 (5), have cited examples of arsenate-forming processes. High arsenic retention data are reported upon roasting of the arsenic-containing material by choosing roasting parameters in a way to form iron arsenate or calcium arsenate. Choice of such parameters resulted in arsenic retention instead of arsenic volatilization during roasting. All of these works were carried out at high temperatures in an oxidizing atmosphere.

One of the objectives of this study was to study arsenate formation at much lower temperatures than those mentioned earlier. Another objective was to produce calcium arsenate, iron arsenate, and aluminum arsenate. The following materials were chosen as possible arsenic getters:

1. CaO
2. $CaCO_3$
3. $Ca(OH)_2$
4. Cottrell dust
5. Fly ash
6. Phosphate rock
7. Phosphate slag
8. Copper smelter slag
9. Fe_2O_3
10. $Fe(OH)_3$
11. FeS_2
12. Jarosite
13. Bentonite clay
14. Kaolin clay
15. Al_2O_3
16. $Al(OH)_3$

Arsenic-getters from one to seven contain calcium as a major constituent. Eight to twelve have iron as a major constituent. Compounds thirteen through sixteen contain substantial amounts of aluminum. Cottrell dust, fly ash, phosphate slag, smelter slag, and jarosite are industrial waste products.

Requirements for Arsenates

One of the approaches to fix arsenic is by dissolution of arsenic compounds into the copper smelter reverberatory slag and lead blast furnace slag. The forms of arsenic being used in the dissolution studies are iron arsenates and calcium arsenates. Arsenates are being used as starting materials in the project mainly for their arsenic carrying ability, i.e., they have a low vapor pressure and will not boil out of the system before the slag becomes molten. Flue dust or arsenic oxide cannot be used directly because it will vaporize away from the system before it has a chance to dissolve.

ROASTING PARAMETERS

Specific parameters of time, temperature, and solid-to-solid ratios were determined empirically for each arsenic-gettering compound. Maximum arsenic retention and arsenate formation were considered prerequisites for all the getter compounds.

The flue dust contains substantial amounts of not only arsenic, but such elements as zinc, cadmium, lead, bismuth, antimony, copper, etc. These elements are of economical importance to the smelters. Fixation of arsenic within the flue dust would create problems in the subsequent recovery of these elements. However, due to its inherent volatile nature, arsenic can be effectively separated from the flue dust as volatile As_2O_3 which can then be fixed for ultimate disposal. It has been a past practice on part of many smelters to recover arsenic in this manner. Fixation variables are minimized by using pure arsenic as As_2O_3 with little of contamination by the other constituents. This would happen if the flue dust were to be used in the fixation study. Many interactions take place during roasting of a flue dust. It would be hard to isolate the roasting effect of a getter on arsenic in a flue dust which also varies in composition from day to day and smelter to smelter. For these reasons, emphasis was placed on fixation of arsenic as As_2O_3 in an isolated form, with the result that most of the work under this project is carried out by using arsenic as As_2O_3.

As_2O_3 Starting Material

Technical grade As_2O_3 was used as a starting material. It assayed 99.5 percent as As_2O_3. An X-ray diffraction trace obtained of the sample showed most arsenic to be present as As_2O_3.

METHODS OF CHEMICAL ANALYSIS

Procedure for arsenic analysis was adapted from:

> Furman, N.H., et al., eds. Standard Methods of Chemical Analysis. 6th Ed., D. Van Nostrand Company, Inc., Princeton, New Jersey, 1962.

Other metal analyses were performed using atomic absorption methods of chemical analysis.

SECTION 5

EXPERIMENTAL PROCEDURES

The present investigation of pyrometallurgical techniques for retention and stabilization of arsenic was undertaken in the form of a screening program to determine the ability of a number of compounds to act as arsenic-getters and stabilizers.

Pellet Formation

In the first case, pellets were formed using the smelter flue dust and getter compounds. Proportional amounts were weighed out and mixed. A little water was added to the mixture to form a thick paste. The paste was kneaded and pellets of approximately one half inch diameter were made from the paste by hand rolling. The pellets were assigned identification numbers and then dried at 50°C for 24 hours. The pellets were stored in vials pending roasting experiments.

In the second case, pellets of technical grade As_2O_3 and getter compounds were formed using the same procedure as for the flue dust pellets.

Roasting Experiments

Roasting tests were performed using a standard muffle furnace with a temperature controller. Oxidizing atmosphere in the muffle was obtained by leaving the front door open for all the roasting tests. Details of the roasting tests are given under Roasting Parameters that follow the individual cases of arsenic in flue dust and arsenic in arsenic trioxide.

Arsenic-Getter Compounds (Flue Dust)--

Arsenic-getters tried, in these experiments, were calcium carbonate and cottrell dust to form calcium arsenates; iron sulfide as FeS_2 and copper smelter reverberatory slag to form iron arsenates; and kaolin, bentonite, and aluminum hydroxide to give aluminum arsenates.

Roasting Parameters (Flue Dust)--

Three different parameters of composition, time, and temperature were studied in order to observe arsenic retentions as well as conversions. Composition ratios were in the order of 90, 75, 50, and 25 percent flue dust by weight to the corresponding weights of the getters to obtain 100 percent. Temperatures were controlled at 200°, 300°, and 400°C for a duration of 30 and 120 minutes for each pellet of the mixtures. After the roasting of the pellets was accomplished, individual pellets were ground up, analyzed, and the results summarized.

Arsenic-Getter Compounds (As_2O_3)--

The getters in calcium category were CaO, $Ca(OH)_2$, cottrell dust, fly ash, phosphate rock, and phosphate slag. The average calcium contents of the last four materials were 28, 12, 28, and 32 percent respectively. Calcium oxide and calcium hydroxide were of reagent grade. Iron oxide, $Fe(OH)_3$, and natrojarosite were used to form iron arsenates. Iron content of the jarosite was 15 percent. Iron oxide and iron hydroxide were of reagent grade. Bentonite, kaolin, and Al_2O_3 were used to form aluminum arsenates. Of these, bentonite contained 12 percent aluminum and kaolin contained 21 percent aluminum. Aluminum oxide used was of reagent grade.

Hayward, 1952 (6), has mentioned precipitation of ferric iron, arsenic, and other elements from acid leach solution of zinc ores by using lime and/or lime rock. The precipitate is essentially hydroxides of iron with gypsum and other impurities entrapped into them. This precipitate was obtained in the laboratory by mixing lime with ferric sulfate solution. The precipitate was dried and used as an arsenic-getter.

Roasting Parameters (As_2O_3)

Effects of roasting time, roasting temperature, and composition ratios were studied to observe arsenic retentions and conversions. Roasting periods were of 15 and 30 minute durations at temperatures of 200°, 300°, and 400°C. Composition ratios were 5, 10, 25, 50, and 75 percent by weight of arsenic trioxide.

Arsenic Retention Calculations--

Arsenic retention was calculated from the pellet weight and arsenic amounts in the pellet before roasting and after roasting. One example is given of the calculation:

Compound	Roast time	Roast temp.
75% As_2O_3 + 25% CaO	15 min.	200°C

Weight of unroasted pellet = 4.5811 gm
Weight of roasted pellet = 4.4993 gm
Arsenic in unroasted pellet = 53.14%
Arsenic in roasted pellet = 52.63%
Therefore, % arsenic retention is given by,

$$\frac{\text{gm arsenic roasted pellet } (4.4993 \times .5263)}{\text{gm arsenic unroasted pellet } (4.5811 \times .5314)}$$

$$= \frac{2.37}{2.43} \times 100$$

$$= 97.5\%$$

SECTION 6

RESULTS AND DISCUSSION

FLUE DUST ROASTING TESTS

X-ray diffraction analysis of the flue dust sample shows that most of the arsenic present is in the form of arsenolite, (As_2O_3). Arsenic in this form is highly soluble in water. If the smelter flue dust is disposed of in open dumps, arsenic leaching may occur and may contaminate ground water. For these reasons, a number of arsenic-getters were investigated to identify the compounds that would make arsenic less soluble in water.

Calcium Compounds

Pellets of the flue dust and $CaCO_3$, Table 3, show high retentions of arsenic, although those made with 90 percent flue dust start out with lower retentions. This is understandable from the fact that not enough calcium carbonate is present to getter arsenic. High retentions are obtained only when the amount of calcium carbonate exceeds the one required stoichiometrically as calculated below. Since the flue dust contains other elements which are also reacting with calcium carbonate, excess amounts of this compound would be required to fully getter arsenic.

TABLE 3. ARSENIC RETENTION

No.	% $CaCO_3$	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten.
1	10	90	30	200	13.1	16.0	79.1
2	10	90	120	200	12.4	16.0	71.8
3	10	90	30	300	14.0	16.0	78.9
4	10	90	120	300	13.1	16.0	72.7
5	10	90	30	400	13.4	16.0	73.8
6	10	90	120	400	13.0	16.0	73.8
7	25	75	30	200	12.6	13.2	92.5
8	25	75	120	200	12.7	13.2	90.8
9	25	75	30	300	13.2	13.2	93.7
10	25	75	120	300	12.2	13.2	86.4
11	25	75	30	400	13.8	13.2	96.3
12	25	75	120	400	12.7	13.2	89.0
13	50	50	30	200	8.77	8.8	98.2
14	50	50	120	200	8.94	8.8	97.9
15	50	50	30	300	9.0	8.8	98.8
16	50	50	120	300	8.91	8.8	97.0
17	50	50	30	400	9.04	8.8	97.2
18	50	50	120	400	9.00	8.8	98.7
19	75	25	30	200	4.48	4.5	98.5
20	75	25	120	200	4.5	4.5	97.5
21	75	25	30	300	4.56	4.5	98.9
22	75	25	120	300	4.5	4.5	97.8
23	75	25	30	400	4.52	4.5	98.2
24	75	25	120	400	4.49	4.5	98.0

$$1 \text{ gm flue dust} \times 17.7\% \text{ As } \frac{.177}{74.992} = 0.0024 \text{ moles As}$$

$$3\ CaCO_3 + As_2O_3 + O_2 \rightarrow Ca_3(AsO_4)_2 + 3\ CO_2$$

$$0.0024 \text{ moles As} \times \frac{3 \text{ moles } CaCO_3}{2 \text{ moles As}} \times \frac{100.091 \text{ gm}}{\text{mole } CaCO_3} = 0.36 \text{ gm } (CaCO_3)$$

Stoichiometric amount of calcium carbonate required:

$$\frac{0.36 \text{ gm } CaCO_3 \times 100}{1 \text{ gm flue dust} + .36 \text{ gm } CaCO_3} = 26.5 \text{ W/O}$$

Cottrell dust, which was obtained from a cement manufacturing plant, contains a mixture of $CaCO_3$ and CaO along with some MgO. Although the cottrell dust is high in calcium content (28% Ca or 70% $CaCO_3$) it does not approach the same level in calcium as obtained in pure $CaCO_3$. Arsenic retention is understandably low when nonstoichiometric amounts of calcium are used (Table 4). Retentions do not improve until the cottrell dust builds up to around 50 percent. This is where net calcium content is increasing in the flue dust and is being made available to react with arsenic.

Iron Compounds

Pellets made with FeS_2 (Table 5), show arsenic retentions in much lower ranges than obtained by using calcium compounds. FeS_2 releases sulfur dioxide upon roasting and a great deal of decrepitation of the pellet occurs as the SO_2 escapes from within the pellet, thus creating a large surface area for arsenic volatilization. The evolved sulfur dioxide gas may be helping arsenic, which is also in the vapor state, to volatilize.

The use of copper smelter reverberatory slag was based on the fact that it contains a large amount of iron mainly in the

TABLE 4. ARSENIC RETENTION

No.	% Cottrell Dust	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten.
1	10	90	30	200	9.91	15.96	57.7
2	10	90	120	200	9.55	15.96	55.1
3	10	90	30	300	11.2	15.96	60.6
4	10	90	120	300	11.0	15.96	59.0
5	10	90	30	400	10.75	15.96	60.3
6	10	90	120	400	10.3	15.96	56.8
7	25	75	30	200	10.4	13.0	76.8
8	25	75	120	200	10.5	13.0	75.8
9	25	75	30	300	11.1	13.0	79.7
10	25	75	120	300	11.2	13.0	78.9
11	25	75	30	400	10.9	13.0	75.9
12	25	75	120	400	10.2	13.0	74.1
13	50	50	30	200	7.65	8.6	86.9
14	50	50	120	200	7.6	8.6	88.7
15	50	50	30	300	7.98	8.6	89.3
16	50	50	120	300	7.82	8.6	87.3
17	50	50	30	400	7.87	8.6	88.8
18	50	50	120	400	7.6	8.6	86.7
19	75	25	30	200	4.07	4.3	95.2
20	75	25	120	200	4.11	4.3	93.8
21	75	25	30	300	4.24	4.3	96.5
22	75	25	120	300	4.50	4.3	95.8
23	75	25	30	400	4.19	4.3	96.1
24	75	25	120	400	4.20	4.3	96.8

TABLE 5. ARSENIC RETENTION

No.	% FeS_2	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten.
1	10	90	30	200	10.9	16.69	59.2
2	10	90	120	200	10.2	16.69	55.9
3	10	90	30	300	8.46	16.69	43.5
4	10	90	120	300	10.2	16.69	50.1
5	10	90	30	400	12.37	16.69	61.9
6	10	90	120	400	11.2	16.69	57.3
7	25	75	30	200	8.49	14.4	53.0
8	25	75	120	200	8.6	14.4	52.6
9	25	75	30	300	10.0	14.4	59.5
10	25	75	120	300	9.9	14.4	55.9
11	25	75	30	400	7.04	14.4	40.1
12	25	75	120	400	10.1	14.4	56.8
13	50	50	30	200	8.64	9.9	83.7
14	50	50	120	200	7.4	9.9	68.0
15	50	50	30	300	8.7	9.9	79.0
16	50	50	120	300	8.6	9.9	78.1
17	50	50	30	400	8.85	9.9	78.5
18	50	50	120	400	8.99	9.9	76.8
19	75	25	30	200	--	--	--
20	75	25	120	200	--	--	--
21	75	25	30	300	--	--	--
22	75	25	120	300	--	--	--
23	75	25	30	400	--	--	--
24	75	25	120	400	--	--	--

form of FeO with some Fe_3O_4 accompanying it. From the arsenic retention data of the slag (Table 6), iron is not reacting enough to retain arsenic. Only when the arsenic content of the pellet drops substantially by using the lowest of the flue dust to slag composition, does one see a small increase in arsenic retention.

Aluminum Compounds

Kaolin and bentonite clays were tested as sources of aluminum for reaction with arsenic in the flue dust. Arsenic retentions are lower with kaolin than with bentonite, the latter being a montmorillonite type clay (Tables 7 and 8). With respect to arsenic retention, other than reacting with aluminum in them, some adsorption of arsenic may be occurring. To identify adsorbed arsenic is beyond the scope of this project. Aluminum hydroxide shows higher arsenic retentions (Table 9) than those exhibited by the clays at better than stoichiometric requirement.

X-Ray Diffraction Analysis

X-ray diffraction work on these pellets was not undertaken for two reasons:

1. In the flue dust, arsenic is surrounded by the presence of a multitude of other elements. Upon roasting, reactions are taking place not only between arsenic and the getter, but also between the other elements and the getter. In this case, the influence of the getter upon arsenic depends largely on the degree of the severity of reaction the other elements may have upon the getter. It would have involved too much time to untangle all these reactions.

2. The multiplicity of the X-ray diffraction analysis was staggering.

TABLE 6. ARSENIC RETENTION

No.	% Slag+FD	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten.
1	10	90	30	200	8.28	14.8	50.1
2	10	90	120	200	7.9	14.8	43.8
3	10	90	30	300	9.36	14.8	52.4
4	10	90	120	300	8.48	14.8	44.3
5	10	90	30	400	9.69	14.8	50.5
6	10	90	120	400	9.6	14.8	50.7
7	25	75	30	200	6.81	12.9	48.8
8	25	75	120	200	6.9	12.9	47.7
9	25	75	30	300	7.54	12.9	51.6
10	25	75	120	300	7.1	12.9	48.4
11	25	75	30	400	9.16	12.9	61.7
12	25	75	120	400	8.0	12.9	53.6
13	50	50	30	200	5.26	8.9	57.0
14	50	50	120	200	5.2	8.9	52.7
15	50	50	30	300	5.64	8.9	57.9
16	50	50	120	300	6.42	8.9	62.2
17	50	50	30	400	5.46	8.9	62.3
18	50	50	120	400	5.6	8.9	63.4
19	75	25	30	200	3.01	4.6	63.7
20	75	25	120	200	2.9	4.6	60.4
21	75	25	30	300	3.35	4.6	70.8
22	75	25	120	300	3.1	4.6	64.3
23	75	25	30	400	3.35	4.6	70.2
24	75	25	120	400	3.05	4.6	63.3

TABLE 7. ARSENIC RETENTION

No.	% Kaolin	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten.
1	10	90	30	200	8.7	15.4	56.5
2	10	90	120	200	9.8	15.4	63.6
3	10	90	30	300	10.57	15.4	68.6
4	10	90	120	300	9.8	15.4	63.6
5	10	90	30	400	9.5	15.4	61.7
6	10	90	120	400	11.2	15.4	72.7
7	75	75	30	200	7.93	12.6	62.9
8	75	75	120	200	9.3	12.6	73.8
9	75	75	30	300	8.81	12.6	69.9
10	75	75	120	300	9.0	12.6	71.4
11	75	75	30	400	10.04	12.6	79.7
12	75	75	120	400	9.4	12.6	74.6
13	50	50	30	200	5.89	8.7	67.7
14	50	50	120	200	5.69	8.7	66.2
15	50	50	30	300	8.28	8.7	95.2
16	50	50	120	300	6.8	8.7	79.1
17	50	50	30	400	6.13	8.7	70.5
18	50	50	120	400	6.9	8.7	80.2
19	75	25	30	200	3.09	4.18	73.9
20	75	25	120	200	3.06	4.18	73.2
21	75	25	30	300	3.7	4.18	88.5
22	75	25	120	300	3.1	4.18	74.2
23	75	25	30	400	3.12	4.18	74.6
24	75	25	120	400	3.48	4.18	83.3

TABLE 8. ARSENIC RETENTION

No.	% Bentonite	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten
1	10	90	30	200	10.2	15.1	58.2
2	10	90	120	200	9.40	15.1	55.6
3	10	90	30	300	9.52	15.1	55.3
4	10	90	120	300	9.10	15.1	53.4
5	10	90	30	400	10.29	15.1	56.3
6	10	90	120	400	10.40	15.1	55.7
7	25	75	30	200	9.12	12.6	68.9
8	25	75	120	200	8.90	12.6	67.2
9	25	75	30	300	8.81	12.6	65.7
10	25	75	120	300	8.60	12.6	59.4
11	25	75	30	400	9.66	12.6	67.0
12	25	75	120	400	9.2	12.6	64.2
13	50	50	30	200	7.48	8.5	79.6
14	50	50	120	200	9.26	8.5	79.6
15	50	50	30	300	7.22	8.5	76.1
16	50	50	120	300	6.5	8.5	65.0
17	50	50	30	400	6.33	8.5	72.1
18	50	50	120	400	6.8	8.5	66.5
19	75	25	30	200	3.75	3.9	92.5
20	75	25	120	200	3.7	3.9	87.6
21	75	25	30	300	3.95	3.9	93.2
22	75	25	120	300	3.8	3.9	88.5
23	75	25	30	400	3.50	3.9	80.5
24	75	25	120	400	3.41	3.9	78.4

TABLE 9. ARSENIC RETENTION

No.	% Al(OH)$_3$	% Flue Dust	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate.	% As Reten.
1	10	90	30	200	9.4	15.1	55.5
2	10	90	120	200	9.1	15.1	53.5
3	10	90	30	300	11.1	15.1	61.4
4	10	90	120	300	10.4	15.1	56.5
5	10	90	30	400	10.9	15.1	60.8
6	10	90	120	400	3.95	15.1	54.1
7	25	75	30	200	10.45	12.5	74.2
8	25	75	120	200	10.3	12.5	72.1
9	25	75	30	300	10.75	12.5	78.9
10	25	75	120	300	11.1	12.5	72.4
11	25	75	30	400	10.59	12.5	70.6
12	25	75	120	400	10.50	12.5	68.9
13	50	50	30	200	7.62	8.6	82.9
14	50	50	120	200	7.40	8.6	81.7
15	50	50	30	300	8.10	8.6	87.8
16	50	50	120	300	8.0	8.6	84.5
17	50	50	30	400	8.28	8.6	86.9
18	50	50	120	400	9.25	8.6	85.6
19	75	25	30	200	3.78	4.8	72.0
20	75	25	120	200	3.54	4.8	70.8
21	75	25	30	300	3.72	4.8	76.6
22	75	25	120	300	4.02	4.8	72.7
23	75	25	30	400	3.79	4.8	73.3
24	75	25	120	400	4.45	4.8	72.9

As_2O_3 ROASTING TESTS

Experiments to fix arsenic within the flue dust would also fix the other metal values in it, thus diluting the effectiveness of an arsenic-getter. Also, these metal values are lost for any subsequent recovery. Considering these matters, arsenic-getters were studies to retain arsenic by using pure arsenic trioxide with the getters. Most of the arsenic in flue dust is in the form of As_2O_3. This is easily liberated from the flue dust by applying a low temperature roast. By using As_2O_3 from which to getter arsenic, more experimental control is achieved on roasting experiments.

Arsenate Formation--

Arsenic trioxide has a high vapor pressure even at moderately low temperatures. Its normal boiling point is approximately 450°C. Arsenic, in this case, is lost upon roasting if it is not tied up in the arsenate form. If, however, pellets are formed from a mixture of getter, arsenic trioxide, and water, the vaporized arsenic would, most likely, react with the getter to form an arsenate of that getter.

Calcium Compounds--Using calcium compounds as getters, high arsenic retentions are obtained. In the case of CaO and $Ca(OH)_2$, most of the arsenic remains in the roasted pellet. This, most likely, is as calcium arsenate and unvolatilized arsenic trioxide. X-ray diffraction analysis of 1:1 mixture of the roasted product showed no identifiable As_2O_3 peaks; however, the presence of

$Ca_3(AsO_4)_2$ was confirmed. The retention data are given in Tables 10 and 11. Stoichiometric calcium compound requirements for possible calcium arsenates formation were calculated as 46 W/O for CaO, 53 W/O for $Ca(OH)_2$, and 60 W/O for $CaCO_3$ which is the main form of calcium in the cottrell dust. Cottrell dust also showed high arsenic retentions although arsenate formation was not confirmed from X-ray diffraction trace. Arsenic retention is dependent on the composition. Only when large ratios of cottrell dust to arsenic are employed do significant retentions occur (Table 12).

Power plant fly ash is, in many cases, scrubbed with additional lime before disposal. The fly ash used in the experiments shows a calcium concentration of 12 percent. It appears that the fly ash was not scrubbed with lime in this case. As to what form the calcium is occurring in the fly ash cannot be determined from the X-ray trace. The roasting tests do not show good retentions. Arsenic is lost by volatilization. These retention data are shown in Table 13.

Phosphate ore and phosphorus slag are high in calcium but arsenic retentions are low. An X-ray analysis of the phosphate ore indicates that calcium is occurring as fluorapatite, $Ca_3(PO_4)_2CaF_2$. The phosphorus slag shows calcium to occur as calcium silicate, $CaSiO_3$. In either case, calcium is not being made available to react with arsenic. Arsenic is lost by volatilization from the pellets when heated. Retentions are poor at

TABLE 10. ARSENIC RETENTION

No.	% CaO	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.02 (3.00)	3.04	97.3 (97.1)
2			30	200	2.88 (2.80)		93.4 (93.0)
3			15	300	3.13 (3.06)		99.3 (99.3)
4			30	300	2.95 (3.02)		96.3 (98.7)
5			15	400	3.05 (3.01)		99.5 (98.3)
6			30	400	3.15 (3.15)		97.9 (97.8)
7	90	10	15	200	--	--	--
8			30	200	—		--
9			15	300	--		--
10			30	300	--		--
11			15	400	--		--
12			30	400	—		—
13	75	25	15	200	15.0	14.7	99.9
14			30	200	15.0		97.5
15			15	300	15.0		98.3
16			30	300	15.2 (15.1)		97.7 (97.6)
17			15	400	15.1		99.4
18			30	400	15.1 (15.0)		98.0 (97.5)
19	50	50	15	200	33.1 (32.8)	33.1	98.9 (98.5)
20			30	200	33.5 (32.5)		95.9 (94.7)
21			15	300	33.7		95.9
22			30	300	32.5 (31.6)		93.2 (93.1)
23			15	400	33.6		97.4
24			30	400	33.4 (33.8)		96.0 (97.3)
25	25	75	15	200	52.6	53.1	97.4
26			30	200	52.7		96.3
27			15	300	52.8		98.7
28			30	300	51.7		92.1
29			15	400	52.0		90.3
30			30	400	52.3		85.8

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 11. ARSENIC RETENTION

No.	% Ca(OH)$_2$	% As$_2$O$_3$	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.75(3.72)	3.71	98.7 (98.5)
2			30	200	3.72(3.73)		97.9 (98.0)
3			15	300	3.75		98.8
4			30	300	3.71		97.6
5			15	400	3.75		98.5
6			30	400	3.74		97.8
7	90	10	15	200	7.38(7.45)	7.25	98.8 (99.1)
8			30	200	7.35(7.3)		98.2 (98.0)
9			15	300	7.41		99.2
10			30	300	7.38		98.7
11			15	400	7.47		99.3
12			30	400	7.40		98.4
13	75	25	15	200	19.0	18.2	99.2
14			30	200	18.9		98.3
15			15	300	19.3		99.8
16			30	300	19.4		98.8
17			15	400	19.3		99.0
18			30	400	20.3		98.7
19	50	50	15	200	38.8 (39.1)	36.4	98.9 (98.7)
20			30	200	39.2 (39.2)		98.0 (98.3)
21			15	300	39.5		98.3
22			30	300	40.1		98.0
23			15	400	40.1		98.9
24			30	400	39.4		97.6
25	25	75	15	200	57.6	57.9	99.2
26			30	200	57.1		98.0
27			15	300	57.8		97.6
28			30	300	57.1		94.5
29			15	400	57.7		92.9
30			30	400	54.3		84.1

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 12. ARSENIC RETENTION

No.	% Cottrell Dust	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.98	4.09	94.1
2			30	200	3.99 (4.15)		93.9 (94.8)
3			15	300	4.09		97.4
4			30	300	4.02		95.4
5			15	400	4.04 (4.01)		95.7 (96.9)
6			30	400	4.0		94.5
7	90	10	15	200	7.11	7.39	94.9
8			30	200	7.13 (7.28)		93.4 (93.0)
9			15	300	7.15		94.6
10			30	300	7.10		93.5
11			15	400	7.39		97.1
12			30	400	7.18 (7.02)		94.3 (92.9)
13	75	25	15	200	17.5	18.5	94.1
14			30	200	17.5		92.6
15			15	300	17.8		94.2
16			30	300	17.4		91.9
17			15	400	18.9		98.2
18			30	400	18.6		94.0
19	50	50	15	200	35.7	36.4	97.5
20			30	200	35.4		95.2
21			15	300	35.4		94.7
22			30	300	35.2		92.2
23			15	400	34.9 (32.7)		88.4 (80.1)
24			30	400	36.5 (38.1)		66.2 (62.7)
25	25	75	15	200	53.9	53.8	99.3
26			30	200	53.9		98.9
27			15	300	54.1		97.0
28			30	300	53.8		95.5
29			15	400	52.5		83.0
30			30	400	53.0		48.4

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 13. ARSENIC RETENTION

No.	% Fly Ash	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.48	3.53	97.9
2			30	200	3.43		96.0
3			15	300	3.23		90.3
4			30	300	3.19		89.6
5			15	400	3.19		88.8
6			30	400	2.99		83.2
7	90	10	15	200	7.40	7.40	99.6
8			30	200	7.03		92.9
9			15	300	7.0		91.8
10			30	300	5.82 (5.51)		75.3 (71.5)
11			15	400	5.15		66.8
12			30	400	3.92 (3.77)		50.0 (48.1)
13	75	25	15	200	17.3	17.6	97.9
14			30	200	17.1		96.3
15			15	300	16.4		92.1
16			30	300	15.4		85.7
17			15	400	14.5		78.9
18			30	400	11.8		59.8
19	50	50	15	200	34.9	35.1	98.9
20			30	200	34.3		94.9
21			15	300	33.2		92.3
22			30	300	33.2		90.9
23			15	400	31.7		85.9
24			30	400	28.9		63.9
25	25	75	15	200	53.8	54.4	98.5
26			30	200	53.8		97.5
27			15	300	52.2		93.7
28			30	300	51.4		85.3
29			15	400	52.5		97.7
30			30	400	51.3		59.7

Numbers in parenthesis are the roasting results of a duplicate run.

higher temperatures. These retentions data are presented in Tables 14 and 15. X-ray diffraction analysis showed no arsenate formation.

Iron Compounds--Iron oxide (Fe_2O_3), iron hydroxide [$Fe(OH)_3$], and natrojarosite were used as getters. Fe_2O_3 used was of reagent grade while $Fe(OH)_3$ was precipitated in the laboratory. Only a portion of the pellet data is presented for $Fe(OH)_3$. Natrojarosite is a common byproduct in the zinc industry although this compound was precipitated in the laboratory.

For Fe_2O_3, arsenic retentions are consistently low upon roasting at higher temperatures. Arsenic is lost by volatilization. The retention data are shown in Table 16. X-ray diffraction analysis does not indicate any iron arsenate formation. In the case of $Fe(OH)_3$, only one group of pellets is presented. Although retentions in this case are higher than those shown by the Fe_2O_3 group, no indication of iron arsenate formation is found from the X-ray diffraction analysis (Table 17).

It shall be noted here, though, that iron arsenate precipitated in the laboratory from aqueous state also does not show its presence on the X-ray diffraction trace as the precipitate is amorphous. Only by heating that precipitate to around 900°C is the presence of iron arsenate noted.

Natrojarosite, $(Na,K)Fe_3(SO_4)_2(OH)_6$, loses SO_2 upon heating. Arsenic is lost, along with sulfur dioxide, when the latter escapes from the pellet. Arsenic retentions in this case also were poor. These data for the natrojarosite are presented in Table 18.

TABLE 14. ARSENIC RETENTION

No.	% Phosphate Rock	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.53	3.66	95.6
2			30	200	3.44		92.9
3			15	300	3.19		86.1
4			30	300	2.42		63.0
5			15	400	1.53 (1.58)		40.6 (41.7)
6			30	400	1.54 (1.65)		40.3 (40.0)
7	90	10	15	200	7.02	7.35	94.9
8			30	200	7.07		93.0
9			15	300	6.39		82.1
10			30	300	5.87		73.2
11			15	400	2.73 (2.18)		35.8 (28.6)
12			30	400	1.88 (1.52)		23.2 (18.8)
13	75	25	15	200	18.3	18.7	97.6
14			30	200	18.2		96.6
15			15	300	16.5		85.3
16			30	300	16.3 (14.4)		82.8 (73.1)
17			15	400	11.6 (8.54)		54.4 (40.2)
18			30	400	2.22 (2.98)		8.99(11.9)
19	50	50	15	200	35.45	36.5	96.9
20			30	200	35.1		95.5
21			15	300	35.8		93.2
22			30	300	30.8		68.3
23			15	400	26.3		55.4
24			30	400	29.0		38.5
25	25	75	15	200	54.7	54.6	99.9
26			30	200	54.4		99.5
27			15	300	54.2		97.1
28			30	300	50.9		72.9
29			15	400	50.8		67.8
30			30	400	48.1		25.6

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 15. ARSENIC RETENTION

No.	% Phosphate Slag	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	.344	3.62	94.4
2			30	200	3.41		93.8
3			15	300	2.69		73.3
4			30	300	2.19 (1.5)		56.9 (40.0)
5			15	400	1.00 (1.2)		26.1 (31.3)
6			30	400	.47 (.44)		12.3 (11.6)
7	90	10	15	200	7.16	7.18	99.4
8			30	200	7.05		97.4
9			15	300	5.16 (5.83)		70.9 (80.1)
10			30	300	4.60 (4.27)		63.2 (58.7)
11			15	400	2.15 (0.68)		27.1 (8.56)
12			30	400	1.11		14.0
13	75	25	15	200	17.5	18.1	96.8
14			30	200	15.4		84.6
15			15	300	14.1		74.7
16			30	300	12.6		63.4
17			15	400	4.91		21.8
18			30	400	.82		3.42
19	50	50	15	200	35.8	36.2	98.3
20			30	200	34.8		95.1
21			15	300	32.4		82.1
22			30	300	30.7		61.0
23			15	400	23.2		45.7
24			30	400	5.9		8.6
25	25	75	15	200	54.4	54.4	99.1
26			30	200	54.2		97.3
27			15	300	51.3		89.9
28			30	300	50.6		76.2
29			15	400	47.9		55.6
30			30	400	47.2		52.4

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 16. ARSENIC RETENTION

Table 16. Arsenic Retention

No.	% Fe_2O_3	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.49	3.81	91.5
2			30	200	3.54		89.1
3			15	300	1.95		50.2
4			30	300	1.02 (1.05)		25.7 (26.6)
5			15	400	1.16 (1.26)		29.3 (31.6)
6			30	400	1.09 (1.07)		27.6 (27.3)
7	90	10	15	200	7.33	7.58	96.7
8			30	200	7.27		95.4
9			15	300	5.35		69.2
10			30	300	1.97		24.9
11			15	400	1.83		22.0
12			30	400	1.26		15.7
13	75	25	15	200	18.0	18.4	97.9
14			30	200	18.2		98.5
15			15	300	13.9		75.1
16			30	300	12.3		66.9
17			15	400	5.12		22.3
18			30	400	1.42		5.9
19	50	50	15	200	35.8	36.7	97.6
20			30	200	35.5		96.6
21			15	300	35.9		94.5
22			30	300	35.2		77.3
23			15	400	34.0		77.3
24			30	400	12.3		22.3
25	25	75	15	200	54.3	57.4	94.6
26			30	200	52.9		91.7
27			15	300	52.2		86.1
28			30	300	49.0		67.6
29			15	400	49.1		60.4
30			30	400	40.8		31.8

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 17. ARSENIC RETENTION.

No.	% Fe(OH)$_3$	% As$_2$O$_3$	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200			
2			30	200			
3			15	300			
4			30	300			
5			15	400			
6			30	400			
7	90	10	15	200			
8			30	200			
9			15	300			
10			30	300			
11			15	400			
12			30	400			
13	75	25	15	200			
14			30	200			
15			15	300			
16			30	300			
17			15	400			
18			30	400			
19	50	50	15	200	35.2	34.8	99.8
20			30	200	34.8		98.0
21			15	300	35.9		96.3
22			30	300	30.0		71.5
23			15	400	30.4		65.3
24			30	400	30.6		64.7
25	25	75	15	200			
26			30	200			
27			15	300			
28			30	300			
29			15	400			
30			30	400			

TABLE 18. ARSENIC RETENTION

No.	% Jarosite	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.89	3.81	93.2
2			30	200	3.69		83.6
3			15	300	3.48		80.1
4			30	300	2.69		59.7
5			15	400	2.58		56.2
6			30	400	2.62		55.6
7	90	10	15	200	7.45	7.61	92.1
8			30	200	7.12		83.6
9			15	300	6.67		79.1
10			30	300	4.37		47.8
11			15	400	4.09		41.9
12			30	400	3.86		40.0
13	75	25	15	200	20.0	20.2	98.7
14			30	200	18.7		83.5
15			15	300	18.6		83.3
16			30	300	11.2 (11.5)		42.8 (44.2)
17			15	400	9.09 (8.89)		30.6 (29.9)
18			30	400	5.08 (5.04)		17.3 (17.2)
19	50	50	15	200	37.4	38.0	93.7
20			30	200	37.7		91.3
21			15	300	39.5		91.1
22			30	300	37.9		76.3
23			15	400	35.2		52.0
24			30	400	36.2		44.4
25	25	75	15	200	55.6	55.2	98.6
26			30	200	55.8		97.9
27			15	300	56.0		97.9
28			30	300	53.2		85.1
29			15	400	52.5		69.9
30			30	400	37.9		22.0

Numbers in parenthesis are the roasting results of a duplicate run.

Aluminum Compounds--Al_2O_3 is too inert to react with arsenic to form aluminum arsenate. Any arsenic retained is as a result of the entrapment. Bentonite shows high arsenic retentions. These retentions are mysterious as no aluminum arsenate is detected by the X-ray diffraction analysis. Arsenic substitution on the clay matrix by some other element cannot be argued favorably as experiments were not carried out to prove it. Kaolin does not show high retentions; neither does it show aluminum arsenate formation. The retention data are presented in Tables 19, 20, and 21.

Precipitate of $Fe(OH)_3$ with Gypsum--Use of this precipitate was prompted by the fact that arsenic is removed during the zinc leach solution purification by adding lime or limerock for neutralization. Precipitation of $Fe(OH)_3$ takes place along with gypsum, aluminum, arsenic, and antimony. The precipitate is controversial in the sense some claim the arsenic is precipitated in the arsenate form while others claim it is adsorbed on the $Fe(OH)_3$ matrix, $Fe(OH)_3$ merely acting as a carrier of arsenic. This precipitate was prepared in the laboratory by adding enough lime to 28 gm/liter solution of $Fe_3(SO_4)_2$ to raise its pH to 5.4. The pellets were then prepared by mixing arsenic with dried precipitate. Arsenic retentions are shown in Table 22. Although still lower in comparison with the calcium compounds, they were better than those achieved by using Fe_2O_3.

Some Remarks on Pelletization

The flue dust is very fine in the particle size. A substantial part of it passes through a 400 mesh sieve. Mixing of the

TABLE 19. ARSENIC RETENTION

No.	% Kaolin	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	2.95	3.67	80.4
2			30	200	2.61		71.1
3			15	300	2.85		77.7
4			30	300	1.65		45.0
5			15	400	.79		21.5
6			30	400	.78		21.3
7	90	10	15	200	--	--	--
8			30	200	--	--	--
9			15	300	--	--	--
10			30	300	--	--	--
11			15	400	--	--	--
12			30	400	--	--	--
13	75	25	15	200	17.5	18.1	96.5
14			30	200	15.2		84.1
15			15	300	16.4		90.6
16			30	300	10.4		57.5
17			15	400	4.29		23.7
18			30	400	1.57		8.7
19	50	50	15	200	35.6	36.9	96.6
20			30	200	35.3		95.7
21			15	300	33.2		90.1
22			30	300	29.8		80.8
23			15	400	22.6		61.4
24			30	400	2.34		6.3
25	25	75	15	200	--	--	--
26			30	200	--	--	--
27			15	300	--	--	--
28			30	300	--	--	--
29			15	400	--	--	--
30			30	400	--	--	--
					--	--	--

TABLE 20

ARSENIC RETENTION

No.	% Bentonite	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.33	3.33	97.5
2			30	200	3.26 (3.56)		95.0 (96.9)
3			15	300	3.19		92.1
4			30	300	3.23		91.8
5			15	400	3.27		90.8
6			30	400	3.09 (3.03)		85.0 (82.7)
7	90	10	15	200	7.07	7.39	94.4
8			30	200	7.12		93.9
9			15	300	7.16 (7.30)		93.9 (94.8)
10			30	300	6.67		87.5
11			15	400	6.74 (7.1)		82.8 (88.1)
12			30	400	6.85		87.7
13	75	25	15	200	18.5	18.6	99.0
14			30	200	18.6		98.2
15			15	300	16.8		88.5
16			30	300	18.6		85.2
17			15	400	17.2		88.1
18			30	400	16.1		81.9
19	50	50	15	200	36.5	37.0	98.5
20			30	200	36.2		97.3
21			15	300	35.9		96.1
22			30	300	35.3		93.3
23			15	400	33.8		86.9
24			30	400	34.4		86.8
25	25	75	15	200	55.2	56.7	96.7
26			30	200	55.1		96.2
27			15	300	55.1		91.6
28			30	300	55.0		88.8
29			15	400	54.1		79.6
30			30	400	47.3		65.3

Numbers in parenthesis are the roasting results of a duplicate run.

TABLE 21

ARSENIC RETENTION

No.	% Iron Hydroxide with Gypsum	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.35	3.28	93.1
2			30	200	3.69		96.7
3			15	300	3.63		94.2
4			30	300	3.35		85.7
5			15	400	3.56		89.8
6			30	400	3.08		77.9
7	90	10	15	200	7.05	6.63	97.5
8			30	200	7.12		94.7
9			15	300	6.56		84.2
10			30	300	6.04		75.3
11			15	400	4.39		52.4
12			30	400	4.59		56.1
13	75	25	15	200	15.6	15.7	95.2
14			30	200	15.6		92.5
15			15	300	15.6		89.1
16			30	300	14.8		81.5
17			15	400	13.8		69.2
18			30	400	5.27		23.6
19	50	50	15	200	35.0	33.2	98.5
20			30	200	35.8		97.6
21			15	300	32.7		89.4
22			30	300	24.0		62.3
23			15	400	32.4		75.1
24			30	400	5.78		8.59
25	25	75	15	200	52.6	53.0	98.7
26			30	200	53.5		97.2
27			15	300	54.9		96.2
28			30	300	52.0		70.3
29			15	400	54.2		95.5
30			30	400	56.6		83.6

TABLE 22

ARSENIC RETENTION

No.	% Al_2O_3	% As_2O_3	Roasting Time Min.	Roasting Temp °C	% As Assayed	% As in orig. mate	% As Reten.
1	95	5	15	200	3.68	3.77	97.4
2			30	200	3.58		93.5
3			15	300	3.48		93.9
4			30	300	3.66 (3.55)		95.5 (93.7)
5			15	400	1.70		43.6
6			30	400	1.08 (1.08)		28.6 (27.5)
7	90	10	15	200	7.03	7.32	96.0
8			30	200	6.60		88.9
9			15	300	5.05		66.7
10			30	300	4.44		57.4
11			15	400	2.79		35.6
12			30	400	1.02		12.6
13	75	25	15	200	16.8	17.8	96.2
14			30	200	15.3		85.7
15			15	300	16.0		88.6
16			30	300	16.7		90.5
17			15	400	15.0		79.8
18			30	400	6.28		28.7
19	50	50	15	200	43.7	43.9	99.5
20			30	200	43.8		99.8
21			15	300	36.3		82.3
22			30	300	34.4		73.0
23			15	400	32.4		66.1
24			30	400	28.2		49.8
25	25	75	15	200	53.4	55.1	96.5
26			30	200	53.7		96.4
27			15	300	54.4		88.0
28			30	300	52.3		66.6
29			15	400	50.5		66.2
30			30	400	43.0		46.6

Numbers in parenthesis are the roasting results of a duplicate run.

flue dust and those arsenic-getters which are floury in nature, such as calcium carbonate, calcium oxide, and hydrated lime, does not produce a homogeneous product. Unbroken globules of the individual materials are always present. Mixing by rolling on a cloth, rolling in jars, or using a blender was tried to achieve maximum homogeneity of the mixture but the mixtures always tended to slime up and stick even in the dry state.

The same problem was encountered when arsenic trioxide and the calcium compounds were used. Mixing did not altogether break these minute globules of one material surrounded by the other. This introduces a sampling error.

In certain cases, such as fly ash, phosphorus slag, and phosphate rock, retentions should be lower using more of As_2O_3 since the substances are not reactive enough to form arsenates and most of the arsenic should volatilize off. Such is not the case. Using these substances in a larger proportion gives a less dense structure as these materials are gritty in nature and the resulting pellet is more porous. Arsenic would escape faster from these pellets.

Arsenic retentions, in the substances that are not reactive chemically to form arsenates, are not true retentions but physical entrapments. They are obtained as a result of the time and temperature relationships associated with roasting, and the bulk density of the pellets.

Arsenic-getter compounds also showed weight loss when roasted individually without arsenic in pelletized form. This information is presented in Tables 23 and 24 as trends since escape of volatile material in the getter compounds is again dependent upon the pellet density.

X-Ray Diffraction Analysis

These data are presented in a tabulated form with explanatory remarks in Tables 25 through 28.

TABLE 23. WEIGHT LOSS UPON ROASTING

No.	Material	Roasting Time Min.	Roasting Temp °C	% Weight Loss
1	Phosphate Rock	15	200	1.47
2		30	200	1.24
3		15	300	.85
4		30	300	.42
5		15	400	1.25
6		30	400	1.21
7	Al_2O_3	15	200	.25
8		30	200	.15
9		15	300	.21
10		30	300	.08
11		15	400	.35
12		30	400	.55
13	Cottrell Dust	15	200	1.65
14		30	200	1.78
15		15	300	1.17
16		30	300	1.16
17		15	400	1.78
18		30	400	2.15
19	Phosphorus Slag	15	200	.41
20		30	200	.32
21		15	300	.26
22		30	300	.22
23		15	400	.33
24		30	400	.67
25	$Ca(OH)_2$	15	200	.79
26		30	200	1.25
27		15	300	1.77
28		30	300	1.50
29		15	400	2.25
30		30	400	2.08

TABLE 24. WEIGHT LOSS UPON ROASTING

No.	Material	Roasting Time Min.	Roasting Temp °C	% Weight Loss
1	Fe_2O_3	15	200	0.35
2		30	200	.15
3		15	300	.14
4		30	300	.23
5		15	400	.20
6		30	400	.20
7	CaO	15	200	1.90
8		30	200	2.11
9		15	300	2.16
10		30	300	2.27
11		15	400	2.25
12		30	400	2.16
13	Bentonite	15	200	1.71
14		30	200	1.68
15		15	300	1.67
16		30	300	1.81
17		15	400	1.94
18		30	400	1.91
19	Jarosite	15	200	9.22
20		30	200	8.45
21		15	300	8.94
22		30	300	9.63
23		15	400	11.3
24		30	400	10.2
25	Fly Ash	15	200	1.00
26		30	200	1.06
27		15	300	1.10
28		30	300	1.51
29		15	400	1.81
30		30	400	1.86

TABLE 25. ROASTING EFFECTS ON ARSENIC-GETTER COMPOUNDS

Compound weight per cent	Roast Time min	Roast Temp °C	Phases identified by X-ray diffraction Technique			Remarks
			As_2O_3	Other	Other	
As_2O_3+CaO	30	200	No	$Ca_3(AsO_4)_2$	–	Calcium arsenate formed in all of the roasts. No evidence of free As_2O_3 found.
50:50	30	300	No	Same	–	
	30	400	No	Same	–	
As_2O_3+Ca(OH)2	30	200	No	$Ca_3(AsO_4)_2$		Calcium arsenate formed in all of the roasts.
50:50	30	300	No	Same		
	30	400	No	Same		
As_2O_3 + Cottrell Dust	30	200	Yes	$CaCO_3$	–	No arsenate formation noticed.
50:50	30	300	No	$CaCO_3$		
	30	400	No	$CaCO_3$		
As_2O_3 + Fly Ash	30	200	Yes	Undetermined		Fly ash seems to be inert to As_2O_3
50:50	30	300	Yes	Undetermined		
	30	400	Yes	Undetermined		

TABLE 26. ROASTING EFFECTS ON ARSENIC-GETTER COMPOUNDS

Compound weight per cent	Roast Time min	Roast Temp °C	Phases identified by X-ray diffraction Technique			Remarks
			As_2O_3	Other	Other	
As_2O_3 + Phosphate Rock 50:50	30	200	yes	Fluoropatite		No arsenic conversion from As_2O_3.
	30	300	yes	Same		
	30	400	No	Same		
As_2O_3 + Phosphate Slag 50:50	30	200	Yes	$CaSiO_3$		No arsenate formation was found in the roasted pallets. The slag is inert and not reactive with As_2O_3.
	30	300	Yes	Same		
	30	400	No	Same		

TABLE 27. ROASTING EFFECTS ON ARSENIC-GETTER COMPOUNDS

Compound weight per cent	Roast Time min	Roast Temp °C	Phases identified by X-ray diffraction Technique			Remarks
			As_2O_3	Other	Other	
As_2O_3+Fe_2O_3 50:50	30	200	Yes	Fe_2O_3		No arsenate formation found.
	30	300	Yes	Same		
	30	400	No	Same		
As_2O_3+Fe(OH)$_3$ 50:50	30	200	--	--		No diffraction analysis performed on roasted samples at either 200°C or 400°C. No arsenate formation noted for sample roasted at 300°C.
	30	300	Yes	Undetermined		
	30	400	--	--		
As_2O_3+Jarosite 50:50	30	200	Yes	Natrojarosite		No arsenate formation noticed.
	30	300	Yes	Same		
	30	400	Yes	Same		
As_2O_3 + iron hydroxide and gypsum 50:50	30	200	Yes	$CaSO_4$		No arsenate formation noted.
	30	300	Yes	same		
	30	400	Yes	undetermined		

TABLE 28. ROASTING EFFECTS ON ARSENIC-GETTER COMPOUNDS

Compound weight per cent	Roast Time min	Roast Temp ^oC	Phases identified by X-ray diffraction Technique			Remarks
			As_2O_3	Other	Other	
As_2O_3 + Bentonite (Montmorillonite type) 50:50	30	200	Yes	Montmorillonite		No arsenate formation noticed.
	30	300	Yes	Same		
	30	400	Yes	Same		
As_2O_3 + Kaotin 50:50	30	200	Yes	Kaolinite		No arsenate formation found.
	30	300	Yes	Same		
	30	400	Yes	Same		
As_2O_2 + Al_2O_3 50:50	30	200	Yes	Al_2O_3		No arsenate formation noticed. Al_2O_3 seems to be inert to As_2O_3.
	30	300	Yes	Same		
	30	400	Yes	Same		

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APPENDIX B

SCALING-UP THE SLAG DISSOLUTION OF ARSENATES

ABSTRACT

Disposal of arsenic in a safe form has long been an environmental problem. It has been shown under the present study that arsenic in arsenate form can be safely disposed off by dissolving it into the waste smelter slag. This laboratory study was being expanded to demonstrate the concept at a bigger scale at a smelter. The demonstration required that a large amount of iron and calcium arsentes be produced in a pilot plant. This scaling-up operation is described with a possible flowsheet and process parameters.

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SECTION 1

INTRODUCTION

Arsenic in its arsenate form can be entraped in a slag matrix. This was successfully shown in the laboratory studies. Arsenic retention is very high and leachability is very small. The concept was viable and could be demonstrated in a larger scale at an actual site. To demonstrate the concept, large quantities of iron and calcium arsenates are required. Calcium arsenate can be produced using a low temperature roasting technique as described in Appendix A. Iron arsenate production was erratic using the same technique. These arsenates could be precipitated using solution chemistry. With a production rate of 500#/day of arsenates in mind, unit processes in hydrometallurgy were studied to produce these arsenates. The specific needs and problem areas are provided. Under the study, the following are discussed for process optimization and design:

1. Precipitation of Arsenates
2. Unit Operation Characteristics

SECTION 2

CONCLUSIONS

In the optimization of iron arsenate production, it was found that the most favorable arsenic removal occurred using 20 to 30 percent excess of ferric sulfate. By using a ferric sulfate concentration of 187.5 gpl and adding this to a 56.3 gpl solution of arsenic (74.25 gpl As_2O_3), in the plus five state, greater than 95 percent of the arsenic can be removed as an iron arsenate. These concentrations were chosen because they allow for easy handling of the resulting slurry and solid liquid separation. The final arsenic concentration of the filtrate, which is dependent upon the amount of NaOH solution used in the neutralization step ranged from 490 to 1000 ppm As. The filtered arsenate contained a large amount of water, between 70 and 75 percent moisture, which had to be driven off to obtain the dry product. The final arsenate contained approximately 25 percent arsenic which is less than the actual expected value. This is due to the coprecipitation of other iron salts and also the insoluble impurities of the ferric sulfate.

This final product is then suitable for dissolution in slags in the final step involved in arsenate retention.

In the production of calcium arsenate, the best arsenic removal occurred at above 12.6 gpl of $Ca(OH)_2$. This was added to a stoichiometric amount of arsenic in the plus five state, added as As_2O_3 previous to its oxidation. The arsenic trioxide concentration was 11.2 gpl As_2O_3. The arsenic and calcium concentrations as above resulted in almost 100 percent arsenic removal. The concentrations of both the arsenic and the calcium hydroxide were then increased, still retaining the stoichiometric balance between the two. A concentration of 150 gpl $Ca(OH_2)$ and its corresponding arsenic value of 133.8 gpl As_2O_3 were used permitting a higher solid:liquid ratio of the final slurry. This concentration was used as the maximum concentration because of the reactivity of H_2O_2 upon its addition to oxidize the As_2O_3, which was almost explosive at higher concentrations. On a large industrial scale one may want to use even a smaller concentration; e.g., 125 gpl $Ca(OH)_2$ and 112.5 gpl As_2O_3, to allow for a condition that will be less reactive during H_2O_2 addition.

The moisture content of the filtered calcium arsenate was not quite as high as that for the iron arsenate, being 60 to 65 percent. The dry arsenate itself contained approximately 25 percent arsenic and this was due to unreacted calcium and other calcium salts. Even though the precipitation boasts approximately 100 percent arsenic removal from the solution, the final concentration is still within 200 to 250 ppm As. This will have to be further treated with lime to decrease the arsenic content.

SECTION 3

RECOMMENDATIONS

It has been shown that the calcium and iron arsenates can be precipitated from solutions removing close to 100 percent of the arsenic. These reactions have been optimized and it is suggested that the figures stated should be used as guidelines in any large scale production of the arsenates. It is also suggested that in any scale up operation the characterization of the physical properties performed earlier is given due consideration during any design work. This work will allow estimates to be made, concerning equipment sizes and capacities, and the relative costs involved.

SECTION 4

MATERIALS AND METHODS

PRECIPITATION OF ARSENATES

Iron arsenate was prepared using arsenic trioxide, sodium hydroxide, hydrogen peroxide, and ferric sulfate. Arsenic trioxide contained 99.5 percent As_2O_3. Sodium hydroxide and hydrogen peroxide were of reagent grade. Ferric sulfate was of commercial grade with 5 percent maximum impurities of which ferrous sulfate was no more than 3 percent.

Calcium arsenate was prepared using calcium hydroxide of commercial grade. The other reagents were the same as in the iron arsenate preparation.

UNIT OPERATION CHARACTERISTICS

Materials used were the same as described in the previous paragraph. In addition, Superfloc 16 and Superfloc 84 were used in the flocculation studies of the arsenate precipitates. The flocculating agents are made by the Cyanimid Company of America.

METHODS OF CHEMICAL ANALYSIS

Chemical analyses were performed using the techniques as described previously in the report.

SECTION 5

EXPERIMENTAL PROCEDURES

PRECIPITATION OF ARSENATES

Precipitation Reactions

In the production of $FeAsO_4$, using As_2O_3 as the original arsenic source, the following reactions have been proposed:

$$As_2O_3 + 4NaOH + 2H_2O_2 \rightarrow 2Na_2HAsO_4 + 3H_2O \qquad (1)$$

$$2Na_2HAsO_4 + Fe_2(SO_4)_3 \rightarrow 2FeAsO_4 + H_2SO_4 + 2Na_2SO_4 \qquad (2)$$

For the calcium arsenate formation the first reaction is the same as for the iron arsenate and then the following reaction is proposed using the resulting sodium arsenate:

$$2Na_2HAsO_4 + 3Ca(OH)_2 \rightarrow Ca_3(AsO_4)_2 + 4NaOH + 2H_2O \qquad (3)$$

Other arsenic compounds were also considered for starting materials; e.g., sodium arsenite ($NaAsO_2$), and calcium arsenite [$Ca(AsO_2)_2$]. The following reactions are proposed to convert these materials into products that can be used to form arsenates.

$$Ca(AsO_2)_2 + 2CaO + 2H_2O_2 \rightarrow Ca_3(AsO_4)_2 + 2H_2O \qquad (4)$$

$$NaAsO_2 + NaOH + H_2O_2 \rightarrow Na_2HAsO_4 + H_2O \qquad (5)$$

The sodium arsenate can then be converted to the iron or calcium arsenate as previously proposed.

Iron Arsenate Formation--

According to reaction (1), to produce stoichiometrically a gram of iron arsenate, 0.25 gram of arsenic trioxide, 0.2 gram of sodium hydroxide, about 27 mls of 35 percent hydrogen peroxide, and a gram of ferric sulfate are required. This is the ideal situation. In laboratory experiments however, stoichiometric amount of ferric sulfate was not enough to react with that of arsenic trioxide. It was found that excess amounts of ferric sulfate were needed.

To determine the excess of ferric sulfate to add to the arsenate solutions, ferric sulfate was dissolved in 1200 ml of water in the proportions shown in Table 1. The solution was stirred for two hours and then a 10 ml sample was removed for iron and free acid determinations. Arsenic trioxide and sodium hydroxide were dissolved in another 1100 ml of water. A 35 percent solution of hydrogen peroxide was then added and allowed to react for 15 to 20 minutes before a 5 ml sample was removed to determine arsenic (III). The ferric sulfate solution was added to the arsenate solution and stirred for approximately 1 hour. Then the pH of each was adjusted to 5.0 using from 70 to 165 ml of 1.0 N NaOH. The solutions were then allowed to sit overnight and were filtered the following morning. The filtrate was passed through a micropore filter after being sampled and was analyzed using atomic absorption.

TABLE 1. REAGENT AMOUNTS USED IN THE DETERMINATION OF THE OPTIMUM EXCESS OF FERRIC SULFATE

$Fe_2(SO_4)_3$ (g)	As_2O_3 (g)	NaOH (g)	H_2O_2 (ml)
18.0	8.2	6.6	25
21.6	8.2	6.6	25
23.4	8.2	6.6	25
25.2	8.2	6.6	25
27.0	8.2	6.6	25

To determine the optimum concentration of $Fe_2(SO_4)_3$, the procedure was the same as previously described. The same initial volumes and sample volumes were used. The only difference being the amount of materials added which is shown below in Table 2. Sodium hydroxide (1N) addition ranged from 75 to 165 ml to bring the solution pH to a value of 5.

TABLE 2. REAGENT AMOUNTS USED TO DETERMINE THE OPTIMUM FERRIC SULFATE CONCENTRATION

$Fe_3(SO_4)_2$ (g)	As_2O_3 (g)	NaOH (g)	H_2O_2 (ml)
15.0	5.45	4.4	4.6
18.8	6.81	5.5	5.8
22.5	8.17	6.6	7.0
26.5	9.53	7.7	8.2
30.0	10.90	8.8	9.4

Calcium Arsenate Formation--

Calcium hydroxide was slurried in a beaker with 1200 ml of water and stirred for 5 minutes. Arsenic trioxide and sodium hydroxide were dissolved in another 1100 ml of water. Enough hydrogen peroxide (35%) was added to oxidize As (III) to As (V).

Residual As (III) was determined with a 10 ml aliquot. This arsenic solution was added to the hydrated lime solution. The samples were stirred for two hours. Solutions were then allowed to sit overnight, filtered, and sampled in the same manner as the iron arsenates. The amounts of reagents added are presented in Table 3.

TABLE 3. REAGENT AMOUNTS USED IN THE DETERMINATION OF THE OPTIMUM CALCIUM HYDROXIDE CONCENTRATION

$Ca(OH)_2$ (g)	As_2O_3 (g)	NaOH (g)	H_2O_2 (ml)
12	9.81	7.93	8.37
15	12.26	9.91	10.46
18	14.72	11.89	12.55
21	17.17	13.87	14.65
24	19.62	15.86	16.74

UNIT OPERATION CHARACTERISTIC

Density Determinations

With the reagents and materials to be used, certain physical characteristics must be determined in order to design equipment and flow rates. Materials densities and then bulk densities are two such properties.

The density of the 35 percent H_2O_2 solution was calculated to allow accurate weight to volume conversions for H_2O_2 addition. The data are shown in Table 4 for 10 ml sample measured into a weighing bottle.

TABLE 4. DENSITY DETERMINATION FOR H_2O_2 (35%)

Weight of vessel and H_2O_2	38.7342	39.0755	39.1846
Weight of vessel	27.4133	27.7486	27.8634
Weight of H_2O_2	11.3209	11.3269	11.3212
Density of H_2O_2	1.1321	1.1327	1.1321

The average density and experimental precision of the 35 percent H_2O_2 solution is 1.132± 0.04.

Determinations for densities and bulk densities for solids were performed as follows: Bulk densities were determined by placing solids into a graduated cylinder and recording the volume. The solids were then packed in the cylinder by tapping on the bottom till they seemed settled to a constant height. The bulk densities of the calcium and iron arsenates were computed this way and the data are presented in Table 5. The experimental precision is ±0.010 g/m^3.

TABLE 5. BULK DENSITIES OF PACKED AND UNPACKED IRON AND CALCIUM ARSENATES AND FERRIC SULFATE

	$Ca_3(AsO_4)_2$	$Fe(AsO_4)$	$Fe_2(SO_4)_3$
Initial volume (ml)	50	53	50
Weight of Sample (g)	24.95	22.34	21.68
Unpacked density (g/cm^3)	0.499	0.422	0.434
Final volume (ml)	35	34	34.8
Packed density (g/m^3)	0.713	0.657	0.623

Densities were performed by water displacement. These data are shown in Table 6 for calcium and iron arsenate. The experimental precision is ±0.04 g/m^3.

TABLE 6. DENSITY DETERMINATIONS FOR IRON AND CALCIUM ARSENATE

	$Ca_3(AsO_4)_2$	$FeAsO_4$
Weight of sample (g)	15	15
Avg. volume of water displacement (ml)	7.23	6.5
Density of solids (g/cm^3)	2.07	2.31

These values may be necessary for the design of storage bins and belt or screw conveyor systems, or in calculating the approximate percent solids of slurries and their flow rates.

Settling Rates

Due to the low percent solids of the resulting arsenate slurries (25 to 35 percent), problems in the filtration step on a pilot scale may arise. Thickening of the solids would alleviate these problems and therefore, batch settling tests were performed. These tests were performed by mixing solids and liquids in a ratio of 1:5 (150 g solids:750 ml H_2O) in a 1000 ml graduated cylinder. The height of the settling interface between the supernatant liquid and the settled solids was recorded as a function of time. A portion of the supernatant liquid was removed, thus increasing the solid-liquid ratio and the test performed again. After the final test, the solids were allowed to settle for 19 hours and the final weight recorded. The thickener area was calculated using the Coe-Clevenger equation,

$$A = \frac{1.333(F-D)\ K}{R}$$

Where A is the area of the thickener (square feet short ton or dry solids/24 hours), F is the initial and D is the final pulp dilution (weight of water/weight of solids), R the settling rate (ft/h), and K is a safety constant ranging from 1.25 to 1.65, Coe and Clevenger, 1916 (1).

To obtain 500 PPD of dry solids, approximately 1750 pounds of iron arsenate and 1310 pounds of calcium arsenate will have to be thickened per day, due to the high percent moistures.

For the calcium arsenate, the actual feed dilution is approximately 2.00. The final dilution is approximately 0.87. The rate will vary from 0.137 ft/h at a solid:liquid ratio of 1:2.67 and from 0.347 ft/h at a solid:liquid ratio of 1:4.67. Therefore, the values of "A" at the two solid:liquid ratios are 26.2 ft^2/TPD and 21.9 ft^2/TPD of dry solids using a K factor of 1.5

Using the iron arsenate, the actual feed dilution is approximately 2.87 and the final dilution is 2.03. The rate varied from 0.120 ft/h with a solid:liquid ratio of 1:4 to 0.277 ft/h at 1:5. Therefore, the "A" value for the iron arsenate ranged from 32.8 ft^2/TPD to 21.4 ft^2/TPD at the two solid:liquid ratios respectively, using a K factor of 1.5. The iron arsenate was almost clayish with respect to its affinity for water and would absorb a large quantity of water, almost one and a half times its own weight. Therefore, in the first batch settling tests, it was hard to achieve a solid:liquid ratio smaller than 1 to 4.

Various tests were performed with flocculating agents. Cyanamid's Superfloc 16 worked excellent and Superfloc 84 worked quite well also. Batch settling tests were performed with different concentrations of Superfloc 16 to determine its effect on the settling rate and thickener area. The experimental results are tabulated in Table 7.

TABLE 7. THE EFFECT OF SUPERFLOC 16 ON SETTLING RATES AND THICKENER AREA

Concentration of Superfloc 16 #/ton		0.0013	0.0027	0.0040
Solid liquid, ratio	max.	1:4	1:4	1:4
	min.	1:5	1:5	1:5
Settling rate (ft/h),	max.	0.36	0.47	0.50
	min.	0.11	0.13	0.14
Thickener area (ft^2/TPD)	max.	35.8	30.3	28.1
	min.	16.5	12.6	11.9

As can be seen in Table 7, the Superfloc does increase the settling rate and will allow for a faster settling time and less thickener area. It may even be favorable to use a higher flocculant concentration, but the economics must be studied. The actual settling test data are presented in Tables 8 through 12, for all the batch settling tests. In Table 8, Tests 2, 3, and 4 were performed after removing 100 ml, 50 ml, and 150 ml of water, respectively. In Tables 9 through 12, Tests 2 and 3 were performed after removing 50 ml and 100 ml of water, respectively.

TABLE 8. BATCH SETTLING TESTS FOR $Ca_3(AsO_4)_2$

Height in ml

1 ml = 0.0138 in.

Time Min.	1	2	3	4
0	750	650	600	450
.5	749	648	599	449
1.0	745	646	597	448
1.5	744	645	593	447
2.0	741	644	592	446
2.5	740	643	591	445
3.0	740	641	590	444
3.5	738	640	590	443
4.0	735	639	589	442
4.5	730	639	588	441
5.0	728	639	587	440
5.5	725	635	585	439
6.0	720	632	583	438
6.5	719	630	581	437
7.0	715	628	580	436
7.5	711	627	579	434
8.0	709	625	577	431
8.5	705	622	574	430
9.0	701	620	571	429
9.5	700	618	570	428
10.0	698	717	568	427
11	690	612	562	425
12	684	608	560	422
13	679	602	555	421
14	671	599	552	420
15	668	595	549	419
16	660	590	545	417
17	655	585	541	414
18	650	580	538	411
19	645	576	533	409
20	640	571	530	405
22	630	565	524	400
24	620	558	518	392
26	611	550	510	386
28	601	541	505	378
30	591	535	400	376
35	570	518	482	369
40	545	500	465	352
45	522	480	448	345
50	500	460	428	340
55	475	440	405	338
60	450	416	390	332
∞				270

Original slurry contains 150 g of $Ca_3(AsO_4)_2$ in 700 ml H_2O

TABLE 9. BATCH SETTLING TEST FOR $FeAsO_4$
Height in ml
1 ml = 0.0138 in.

Time Min.	1	2	3
0	8.00	750	650
.5	7.98	749	649
1	7.93	748	648
1.5	7.90	745	647
2	7.89	744	645
2.5	7.88	742	644
3	7.86	741	643
3.5	7.83	740	642
4	7.81	739	641
4.5	7.80	738	640
5	7.79	737	640
5.5	7.78	736	639
6	7.76	735	639
6.5	7.74	734	638
7	7.72	732	638
7.5	7.70	731	637
8	7.69	730	636
8.5	7.68	729	635
9	7.66	728	634
9.5	7.63	727	633
10	7.61	726	632
11	7.59	724	630
12	7.55	721	629
13	7.51	719	628
14	7.48	717	676
15	7.44	714	624
16	7.42	711	622
17	7.38	709	620
18	7.34	706	619
19	7.30	704	618
20	7.26	701	617
22	7.19	698	613
24	7.10	690	6.10
26	7.02	686	608
28	6.95	680	604
30	6.86	675	600
35	6.65	660	591
40	6.42	645	584
45	6.21	630	575
50	6.00	615	565
55	5.80	600	555
60	5.55	585	545
∞	-	-	355

Original Slurry contains 150 g $Fe(AsO_4)$ in 750 ml of H_2O

TABLE 10. BATCH SETTLING TEST FOR $FeAsO_4$ PLUS 0.0013 lb/ton FLOCCULANT*
Hieght in ml

Time Min.	1	2	3
0	790	740	640
.5	788	739	640
1	783	738	639
1.5	782	737	639
2.0	780	735	639
2.5	779	734	638
3	775	732	637
3.5	772	731	636
4	770	730	635
4.5	768	729	634
5	765	729	632
5.5	762	728	631
6	759	726	630
6.5	756	725	630
7	752	773	630
7.5	750	722	629
8	748	721	629
8.5	744	720	628
9	740	719	627
9.5	738	719	626
10	735	718	625
11	728	716	623
12	720	714	621
13	715	711	620
14	710	710	619
15	704	708	618
16	699	705	617
17	693	700	616
18	688	700	614
19	683	698	612
20	678	695	610
22	669	690	609
24	659	687	
26	650	682	
28	640	678	
30	631	674	
35		663	

* 1 ml of 0.1 gpl flocculant solution
Same solids as before just added back 150 ml of H_2O

TABLE 11. BATCH SETTLING TEST FOR $FeAsO_4$ PLUS 0.0027 lb/ton FLOCCULANT*

Time Min.	Height in ml		
	1	2	3
0	800	750	650
.5	800	748	650
1	800	743	649
1.5	797	740	648
2	792	740	647
2.5	788	739	646
3	784	738	645
3.5	780	736	644
4	776	733	642
4.5	771	731	640
5	768	730	640
5.5	764	729	639
6	760	728	638
6.5	756	726	637
7	751	724	636
7.5	748	722	635
8	744	720	634
8.5	740	719	632
9	736	718	631
9.5	732	717	630
10	728	715	630
11	720	711	629
12	713	709	628
13	705	705	625
14	699	702	622
15	691	700	620
16	685	698	619
17	679	693	618
18	671	690	616
19	665	688	614
20	659	684	611
22	647	678	608
24	633	670	604
26	621	665	600
28	610	658	597
30	600	650	594
35		635	584

* Added another 1 ml of 0.1 gpl Superfloc 16 Solution
Same solids as before just added back 150 ml H_2O

TABLE 12. BATCH SETTLING TESTS FOR $FeAsO_4$ PLUS 0.0040 lb/ton FLOCCULANT*

Time Min.	Height in ml		
	1	2	3
0	800	750	650
.5	798	749	650
1	797	748	649
1.5	790	746	648
2	786	743	645
2.5	780	741	644
3	778	740	642
3.5	773	739	641
4	769	737	640
4.5	765	735	639
5	760	732	639
5.5	766	730	638
6	751	729	637
6.5	749	728	635
7	744	726	634
7.5	740	724	633
8	736	722	632
8.5	731	720	630
9	728	718	630
9.5	723	717	629
10	719	715	628
11	711	711	626
12	704	708	623
13	698	703	621
14	689	699	619
15	681	696	618
16	675	691	616
17	668	689	614
18	660	685	611
19	653	680	609
20	648	678	608
22	634	670	601
24	620	661	599
26	609	655	594
28	596	648	589
30	584	639	586
35			575
40			565
45			555
50			545
55			535
60			523

* Added 1 ml of a 0.1 gpl Superfloc 16 solution
Added 150 ml H_2O to previous solids

Filtration

Another area of consideration in the process of scaling up would definitely be filtration. Various types of filter cloths were investigated and experiments were performed to determine filtration rates and resistances. These tests were performed on the unthickened arsenates that had just been precipitated. The arsenates stayed in suspension quite well and a prior thickening step may not be necessary. This is espcially true with the iron arsenate and may be marginal for the calcium arsenate.

Due to the pH of the arsenate solutions, synthetics were primarily studied to determine a suitable filter cloth. Nylon cloths worked the best as a group, although that was dependent upon the weave or other characteristics of the fabric. Dynel and dacron performed quite well, also. EIMCO's nylon cloth NY-518F was found to work best when both arsenates were taken into consideration; therefore, this cloth was used in the rate determinations.

The following method of obtaining filtration data and the procedure in analyzing the data was proposed by Coates & Pressburg, 1959 (2). This involved the recording of filtrate volume as a function of time. This would allow one to determine the filtration rate and, thus knowing the vacuum, the resistance of the cake and filter medium could be determined. The total resistance is determined by the following equation:

$$\alpha = \frac{KpA^2(-\Delta p)gc}{c\mu} .$$

Where α = total specific resistance, ft/#
A = area of the filter, ft^2
ΔP = pressure drop, $\#/ft^2$
gc = 32.2 ft/s^2
c = # dry solids/ft^3 of filtrate
μ = viscosity, #/ft s
kp = the slope of the line when dt/dv is plotted vs. filtrate volume

In case of a noncompressible cake for a rotary drum or disk filter:

$$V/t_c = A \left(\frac{2(-\Delta p)gcf}{c\ \alpha\ \mu\ t_c}\right)^{1/2} .$$

Where V/t_c = the volume flowrate for 1 cycle, ft^3/s
t_c = time to complete 1 cycle, s
f = the fractional submergence of the filter

Using these equations the specific cake resistance can be determined in filtering a slurry and the approximate amount of surface area required.

The filtration data for the iron and calcium arsenates are shown in Tables 13 and 14, respectively. The dt/dv values are plotted against $\bar{v}$ and the resulting Kp values are determined (Figures 1 and 2). If the amount of dry solids in pounds deposited on the filter per cubic foot of filtrate is C, it can be determined from the following equation:

$$C = \frac{Cs}{1-(1/1-M)-1)Cs/\rho} .$$

Where Cs is the concentration of the solids in the slurry in pounds per cubic foot of liquid feed to the filter, M is the percent moisture of the cake in decimal form, and, ρ is the density of the filtrate.

TABLE 13. FILTRATION DATA FOR IRON ARSENATE

Time (min)	Volume of Filtrate V (ml)	Mean Volume $\bar{v}$ (ml)	$\frac{dt}{dv}$ $\frac{min}{ml}$
00	--	--	--
0.5	52	26	0.0096
1.5	70	61	0.0555
2.0	100	85	0.0167
2.5	115	107.5	0.0333
3.0	126	120.5	0.0909
4.0	144	135	0.0555
5.0	166	155	0.0455
6.0	182	174	0.0625
8.0	235	208.5	0.0377
10.0	255	245	0.100
12.0	288	272	0.0606
15.0	296	292	0.375
18.0	326	311	0.1000
21.0	400	363	0.0405

TABLE 14. FILTRATION DATA FOR CALCIUM ARSENATE

Time (min)	Volume of Filtrate V(ml)	Mean Volume $\bar{v}$ (ml)	dt/dv(min/ml)
0	0	--	--
0.5	135	67.5	0.0037
0.75	175	155	0.0063
1.0	225	200	0.00500
1.5	280	252.5	0.0091
2.0	345	312.5	0.0077
2.5	405	375	0.0083
3.0	455	430	0.0100
3.5	470	462.7	0.0333
4.0	550	510	0.0063
5.0	570	560	0.0500
6.0	575	572.5	0.200
10.0	855	715	0.0140

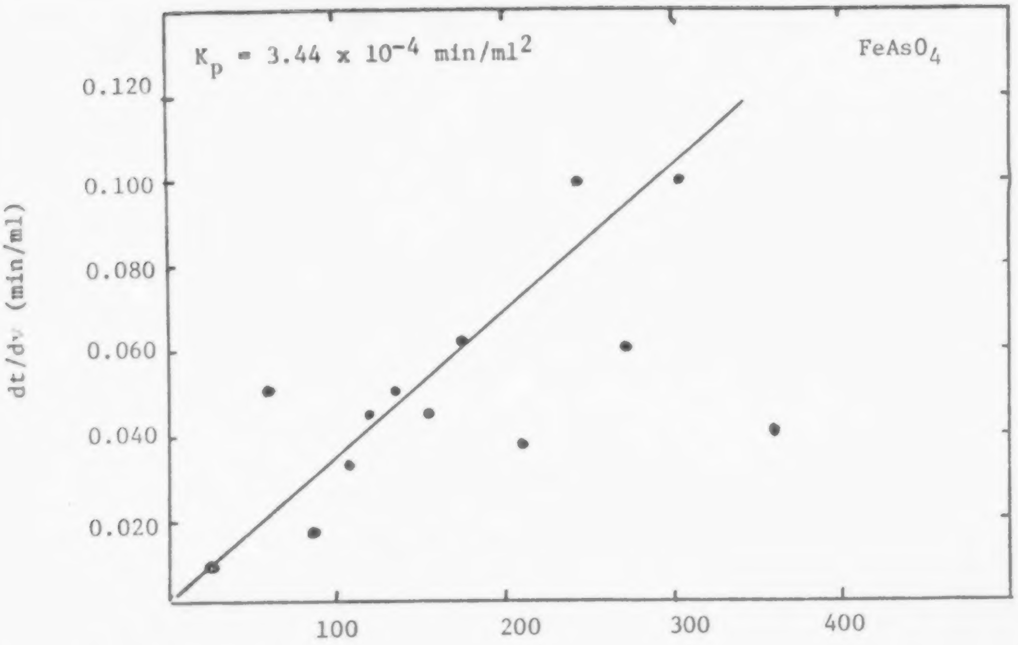


Figure 1. Plot of dt/dv vs. $\bar{v}$ for iron arsenate.

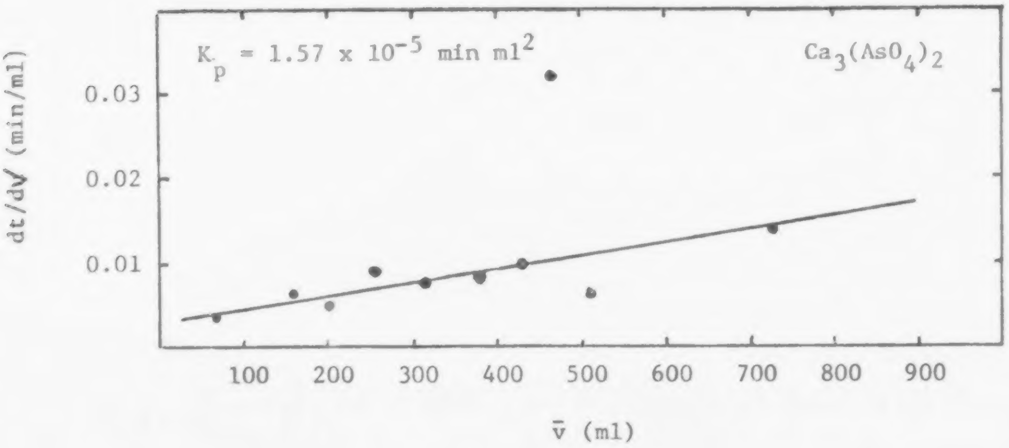


Figure 2. Plot of dt/dv vs. $\bar{v}$ for calcium arsenate.

From the experimental data for the iron arsenate, the percent moisture of the filter cake after a 30 second drying time was approximately 60 percent, and the filtrate's specific gravity was equivalent to 1.03. With a C value equal to 22.35# of dry solid/ft^3 of liquid in the slurry, the corresponding Cs value was 46.72# of dry solids/ft^3 of filtrate. At a pressure drop of 11.5 psi across the filter, the specific cake resistance was determined to be 3.135×10^{11} #/ft. Knowing this cake resistance and assuming a submergence factor of 0.3, the required area for filtration can be determined for a given capacity of dry solids and filter cycle time. The following equation will enable the calculation of filter area in square feet if the cycle time is in seconds and the capacity of dry solids as tons/day:

$$A = 0.324 \text{ TPD } (t_c)^{1/2}, \; (\text{ft}^2).$$

Using the calcium arsenate, the percent moisture was found to be 51.7 percent, while Cs equaled 34.36#/ft^3; therefore, C is equal to 80.9#/ft^3. The resulting specific resistance (α) at 20 psi is equal to 1.44×10^{10} #/ft. Once again the resulting area, ft^2, needed to filter the solids using a 0.3 submergence factor at a 20 psi vacuum can be shown as a function of the TPD of dry solids, and the cycle time in seconds as in the following equation:

$$A = 0.040 \text{ TPD } tc^{1/2}, \; (\text{ft}^2).$$

For both arsenates the high percentage of moisture is due to waters of crystallization or chemically bound water. The ease of handling of the filtered solid seems to suggest this. Both solids filter relatively easily giving beautiful cakes. These cakes can also be blown quite easily from the filter. All things being considered, both arsenate slurries are very receptive to filtration and should not present any unique problems.

Drying

Once the arsenates have been produced they must be dried. The solids must be almost completely dry. This is due to the fact that upon the addition of the arsenate to the high temperature slag, large volumes of steam shall be produced in a short amount of time causing an explosion.

At the speculated throughput of 500#/day of arsenate and using the filter cake moistures, it will require 535# and 750# of water to be evaporated per day for the calcium and iron arsenate, respectively. To dry these solids there would be a heat requirement of 233 Btu and 326 Btu daily.

The heat requirement plus a 10 percent safety factor, to produce a given tonnage per day of dry calcium arsenate is given in the following equation as Btu/h:

$$Q = 38.3\ (TPD),\ Btu/h$$

likewise for the dry iron arsenate:

$$Q = 54.4\ (TPD),\ Btu/h$$

In the drying of the arsenates, it may be advisable to use an indirect method of drying, as the arsenates tend to be powdery. This would prevent dust collection problems and allow for a smoother mode of operation and a lower equipment cost.

SECTION 6

RESULTS AND DISCUSSIONS

PRECIPITATION OF ARSENATES

Iron Arsenate

Initial tests on iron arsenate precipitation were carried out using a S/L ratio of 1:100. The amount of liquid that needed handling was too much. Experiments were carried out to determine a suitable S/L ratio. Solid to liquid ratios from 1:10 to 1:20 fell in a workable range. Finally, to optimize the ferric sulfate concentration, precipitation tests were carried out with ferric sulfate concentration ranging from 100 to 200 grams per liter. A concentration of 150 gpl gave good results. It was found in all of these experiments that excess ferric sulfate was needed to react with and precipitate arsenic from the solutions. Stoichiometric amounts were insufficient. A series of tests was performed to determine the optimum excess amounts and the results are shown in Figure 3. Most of the arsenic is removed by 20 to 30 percent excess of ferric sulfate.

Choosing the amount of excess at 25 percent, further tests were performed to determine the best $Fe_2(SO_4)_3$ concentration. These experimental results are shown in Figure 4. As can be seen there is a gradual increase in the percentage of arsenic removed

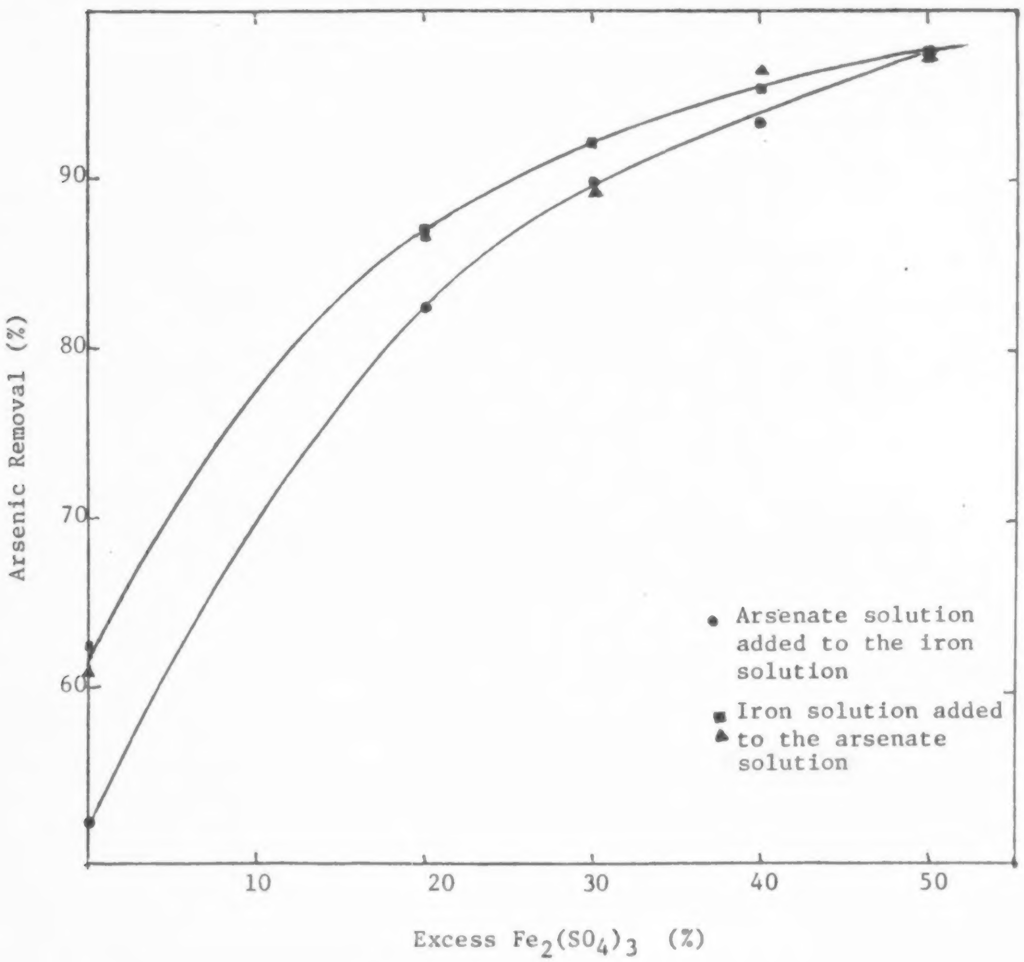
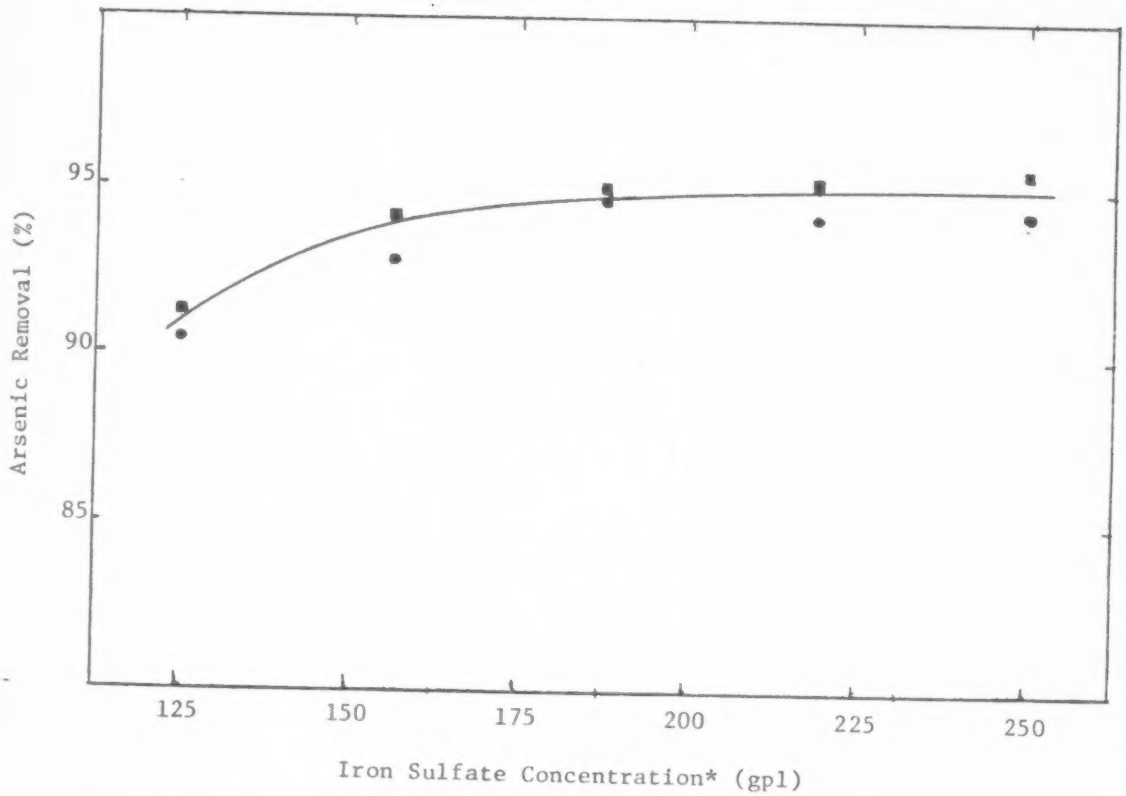


Figure 3. The effect of excess iron sulfate on arsenic removal.



*Stoichiometric iron sulfate required plus 25% excess.

Figure 4. The effect of $Fe_2(SO_4)_3$ concentration on arsenic removal.

as the $Fe_2(SO_4)_3$ concentration increases. This increase leveled out at approximately 95 percent arsenic removal at a $Fe_2(SO_4)_3$ concentration of 150 gpl plus 25 percent excess. This concentration gave maximum removal and a suitable solid-liquid ratio. Depending upon the amount of 0.1N NaOH solution added, the final arsenic concentration could range around 490 to 1000 ppm As. This solution would require additional treatment before it could be disposed of.

It should be noted that pure iron arsenate contains 38.5 percent arsenic. The final arsenate contains only 24 to 25 percent arsenic due to iron hydroxides that precipitate out when the pH is raised, and the iron arsenate is mixed with iron salts.

The final flow sheet and mass balance are shown in Figure 5 for the formation of iron arsenate.

Calcium Arsenate

In the production of calcium arsenate, the concerning factor was $Ca(OH)_2$ concentration. To precipitate the arsenate, lime was added to a concentration ranging from 10 to 20 gpl $Ca(OH)_2$. The experimental data are shown in Figure 6. The percentage of arsenic removed seems to peak out and level off at 12.5 gpl $Ca(OH)_2$. A concentration of 15.0 gpl $Ca(OH)_2$ was chosen for the concentration of batch precipitations to produce the arsenates. This resulted in a 99.7 percent arsenic removal. The arsenic concentration of the final solution was between 200 to 250 ppm As. This solution would have to be further treated to remove arsenic before the solution can be disposed of.

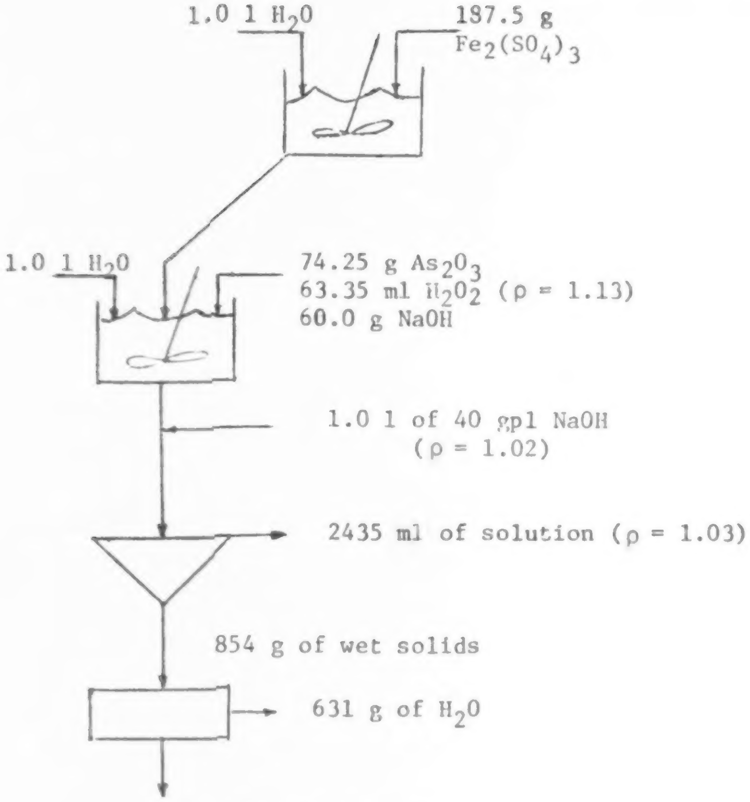
IN

2000
187.5
74.3
60
63.4 (1.13)
1000 (1.02)
3413 g

OUT

2435 (1.03)
631
223
3362 g

Difference of 1.5%



223 g of Iron Arsenate
Theoretical amount of arsenate
that would be produced = 146 g

% Solids of final slurry = 26.00%
% Moisture of final solids = 73.89%
% Arsenic in final solids (dry) = 24.26%

Figure 5. Formation of iron arsenate.

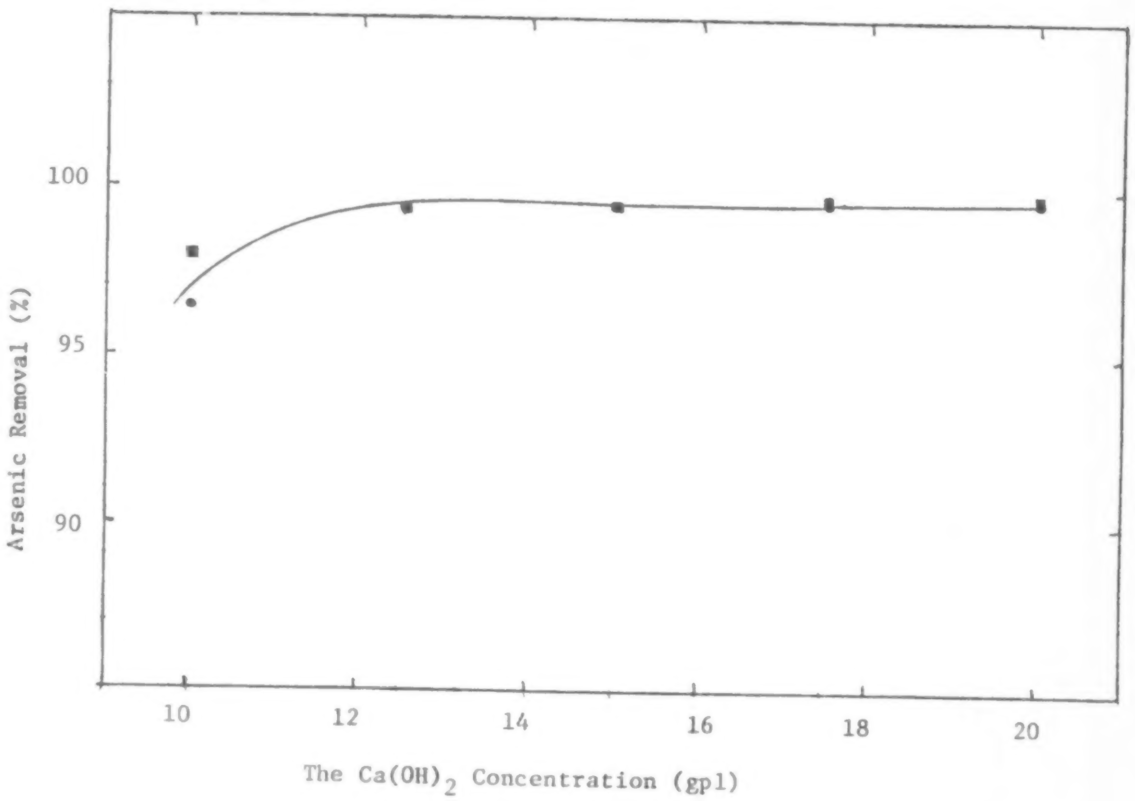


Figure 6. The effect of the Ca(OH)$_2$ concentration on arsenic removal.

In the case of the calcium arsenate, the limiting factor was not the solid:liquid ratio but the reactivity of the solution. Due to the different stoichiometric requirements of the iron and calcium arsenates, the concentration of the arsenic solution to react with the $Ca(OH)_2$ is almost twice the concentration of that to react with the iron sulfate. As a result of this increase in arsenic concentration during the oxidation of the arsenic, the hydrogen peroxide must be added much slower and more carefully.

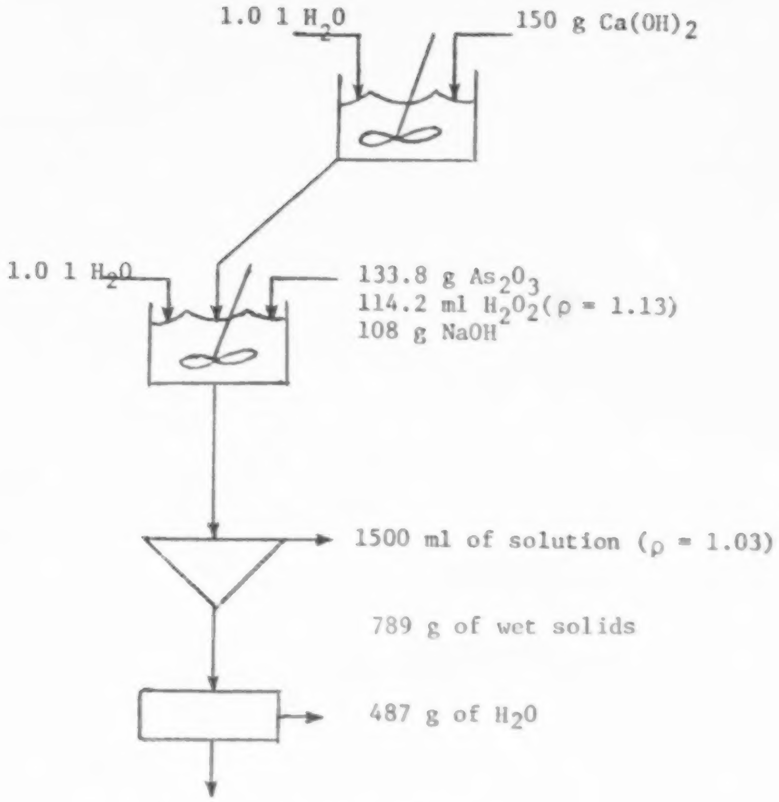
The final precipitate contains unreacted lime as well as the calcium arsenate. This accounts for the final arsenic percentage of 21 to 29 percent as compared to the actual arsenic concentration of 37.8 percent for pure calcium arsenate.

A final flow sheet and mass balance are shown in Figure 7 for the formation of calcium arsenate. This flow sheet is based on 150 gpl of $Ca(OH)_2$ which was as effective in arsenic removal as 15 gpl, and still within the range of safe reactivity when the H_2O_2 was added.

UNIT OPERATION CHARACTERISTICS

Density Determination

The densities and bulk densities of the materials to be used were determined for ease in determining some flow rates and storage capacities. The bulk density of the calcium arsenate is approximately $31\#/ft^3$ while that of the iron arsenate is a little less at about $28\#/ft^3$. With the solids packed their bulk densities increased to $45\#/ft^3$ and $39\#/ft^3$, respectively, and the



IN
2000
150
133.8
108
114.2 (1.13)
2521

OUT
1500 (1.03)
487
302
2344

plus x gram of
Steam on
H_2O_2 addition

302 g of Calcium arsenate
Theoretical amount of calcium
arsenate to be formed = 268 g

% Solids of final slurry = 34.6%
% Moisture of final solids = 61.72%
% Arsenic of final solids (dry) = 21.29%

Figure 7. The formation of calcium arsenate.

material was not as powdery. The actual densities of the arsenates, determined by water displacement, were approximately 129#/ft^3 for $Ca(AsO_4)_2$ and 144#/ft^3 for $FeAsO_4$.

Settling Rates

Both of the arsenates settled well with the settling rates increasing as the solid:liquid ratio was decreasing, this is what is expected. For the calcium arsenate the settling rate went from 0.347 ft/h at a liquid to solid ratio of 4.67, to a settling rate of 0.137 ft/h for a ratio of 2.67. The resulting thickener area required per day's tonnage of dry solids then ranged from 21.9 TPD/ft^2 to 26.2 TPD/ft^2. The 21.9 TPD/ft^2 figure for the liquid:solid ratio of 4.67 is closer to the actual ratio used for the calcium arsenate precipitation which was about 4.9.

The settling rate for the iron arsenate varied from 0.120 to 0.277 ft/h for liquid:solid ratios of 4.0 and 5.0, respectively. Flocculating the arsenate was found to have an effect on the settling rates especially at the higher liquid:solid ratios. Cyanamid's Superfloc 16 was found to be the most effective. The settling rates for the same ratios as above using 0.004#/ton of flocculant were 0.14 and 0.5 ft/h, respectively. This affected the area factors which were 32.8 to 21.4 ft^2/TPD for the flocculated arsenates at the respective liquid:solid ratios by decreasing them to 28.1 and 11.9 ft^2/TPD. The lower figure would be closer to the actual area needed during the iron arsenate precipitation.

Filtration

During the filtration study, it was determined that most of the nylons presented the best filter media, especially EIMCO's NY-518F. This cloth was found to work well with both arsenates. Therefore, rate studies were performed on this cloth. It was determined for the iron arsenate, at 11.5 psi, that the required filter area showed the following relationship to daily throughput of dry solids and the cycle time of the filter:

$$A = 0.324\ (\text{TPD})(t_c)^{1/2},\ (\text{ft}^2)$$

For the calcium arsenate at 20 psi this relationship was:

$$A = 0.040\ (\text{TPD})(t_c)^{1/2},\ (\text{ft}^2)$$

Drying

Once these arsenates were filtered, it became mandatory that they were dried due to the large amount of steam that would be generated upon their addition to the slag if they were not dried. The relationships of the heat requirement to the daily throughput of dry solids desired for the iron and calium arsenate, respectively, are as shown below:

$$Q = 54.4\ (\text{TPD}),\ (\text{Btu/h})$$
$$Q = 38.3\ (\text{TPD}),\ (\text{Btu/h})$$

It has also been suggested that the arsenates be dried using indirect methods to prevent dust collection problems with the arsenate dusts.

FLOWSHEET AND PLANT PRACTICE

A flowsheet was developed on a small pilot scale of 500#/day of dry arsenate. This was to produce all the arsenate needed for the slag dissolution after several months. On the industrial scale, the overall plant practice for arsenate production will follow that of the flowsheet in Figure 8. The arsenate solution and the iron or calcium are mixed separately in stainless steel vessels allowing enough time for dissolution of the soluble solid materials. This resulting solution and the slurry are then pumped into a third larger mixing tank of stainless steel composition. The arsenate precipitation then takes place allowing a retention time of from 1 to 2 hours.

Depending upon whether it is iron or calcium arsenate being produced, the resulting slurries will be treated differently. The iron arsenate slurry will be pumped to another stainless steel vessel where the pH is raised to approximately 5 by adding a NaOH solution. A pH of 5 was found to be optimum for arsenic removal as an iron arsenate. This iron arsenate slurry which has just had its pH adjusted shall be passed along to the filtration stage. The calcium arsenate slurry would be passed on to filtration without any further treatment. A thickening step between the arsenate production and filtration step may be used but it is totally optional, and probably not necessary at all. The filtered solids can then be dried and stored. The filtrate can be recycled back to the original solutions. In the iron arsenate

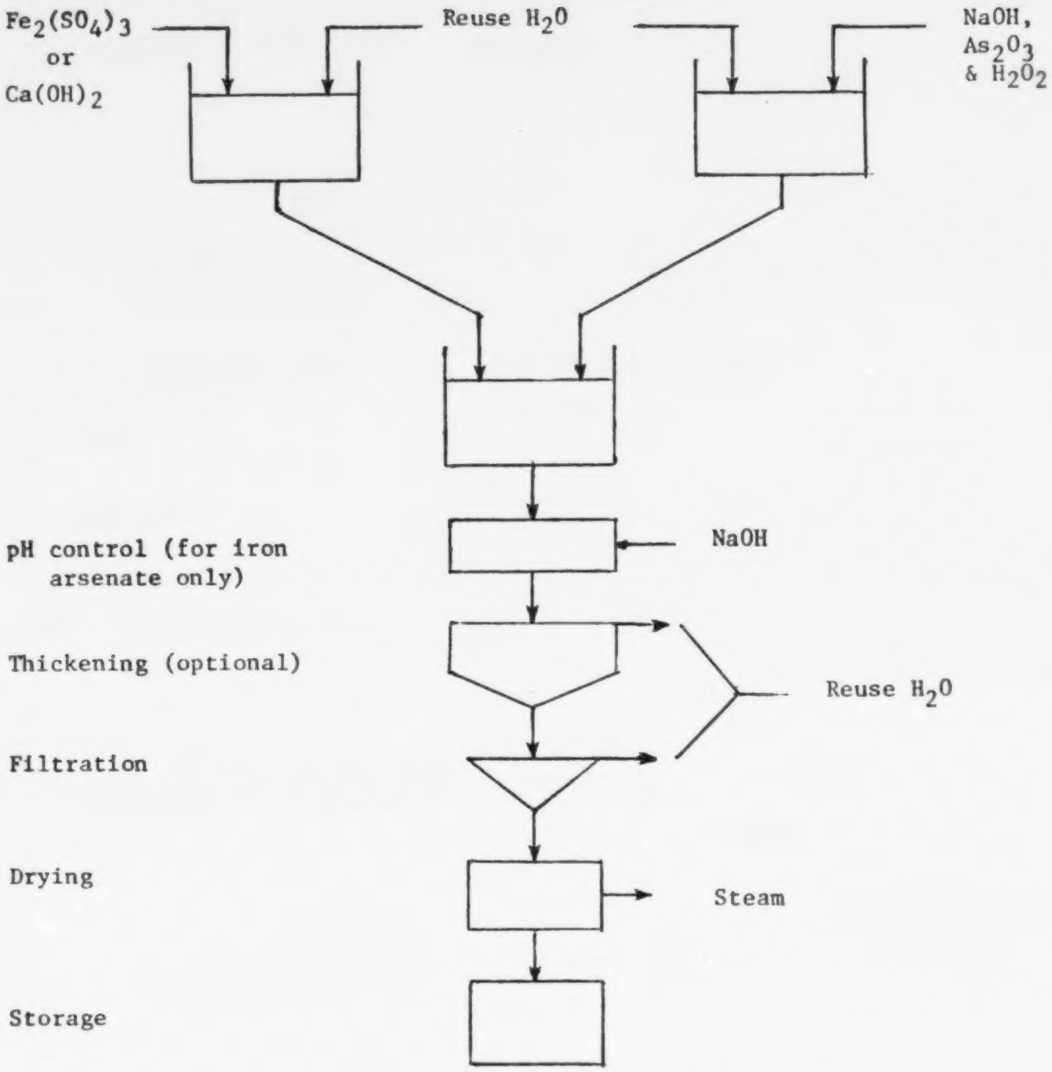


Figure 8. General flowsheet and unit operations.

production, Na_2SO_4 shall build up in the recycle solution. This may be removed by adding lime as in the following equation:

$$Na_2SO_4 + CaO + H_2O \rightarrow CaSO_4\downarrow + NaOH$$

This allows the recycling of a NaOH solution. In the calcium arsenate production, NaOH is regenerated and the final solution can be recycled also.

The actual addition of arsenates to the slag took special consideration. Due to the fineness of the arsenates, pelletization made them much easier to handle and prevented the loss of arsenates due to the suction in the doghouse. Also, a sufficient binder had to be found which would not raise the resulting melting temperature too greatly. One percent by weight sodium silicate addition was chosen for this purpose. Due to the small amount of time required to fill the slag ladle during tapping, approximately 15 minutes, the arsenates had to be added very rapidly. To lower the arsenate feed rate, a third of the required amount of arsenate to be added would be placed in the ladle, before the slag addition. Also to lower dusting and fuming problems and to increase homogenity, it was decided to add the arsenate to the slag near the end of the run, just inside the doghouse. Care must be exercised not to freeze up the run when adding the arsenates.

Some form of storage bin would have to be built on the tapping floor to keep the arsenate pellets nearby for feeding to the doghouse. Conveyance to the doghouse would have to be such that there would be minimum comminution of pellets and still be capable of a high feed rate. This feed rate would be dependent upon the final percentage of arsenic desired in the slag. Assuming a ladle capacity of 30 tons of slag, 25 percent As in the calcium and iron arsenate, 6 minutes to safely feed all the arsenate and striving for a final arsenic percentage of 1 to 5 percent, the maximum feed rate would be 40 TPH.

In the production of large quantities of the arsenates and in their dissolution in slag, it can be seen that a few parameters had to be studied that were not necessary for bench scale production. If it is desired to produce such a large tonnage of arsenates, the preceding information on the material's characteristics may become very useful. Most of the work was concerned with obtaining the dried arsenate material, and further information on arsenate addition to slags would have to be obtained.

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2. Coates, J. and Pressburg, B. S., Chem Eng., Oct. 5, 1959, p. 149.